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THE ELECTRON IN CHEMISTRY.*†

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OXYGEN.

The most fascinating of all magnetic bodies is to my mind oxygen. Here we have one of the simplest of atoms; its atom contains only eight electrons, it is a gas, and therefore in the simplest of all physical states, and yet it alone of all gases is paramagnetic and quite strongly so. Another remarkable thing about it is that innumerable as are the compounds of oxygen there is only one, NO, into which oxygen carries its magnetic properties. This would seem to suggest that the magnetic quality does not arise from some quality intrinsic to the atom, but from some speciality in the arrangement of the colligating electrons in those molecules where it exhibits its magnetic character. The oxygen molecule itself is the most conspicuous example; the arrangement of the electrons may be represented symbolically as two cubes having a face in common, this face being at right angles to the line joining the atoms. If the system were rotating about this line there would be an odd number of square faces in rotation. A rotating square with its electrons would act like

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a current and thus behave like a magneton. Now suppose that the rotation of electrons must be such that adjacent squares rotate in opposite directions, and it is evident that if we start one from rest in one direction, the adjacent one will start in the opposite direction. Suppose then that the electrons in the planes of the squares were rotating so that the rotation in one plane is opposite to that in the adjacent plane, then two of these planes will be rotating in one direction and the third in the opposite, the resulting magnetic effect will be the same as if only one plane rotated, and this will produce a magnet of finite moment.

It might be thought that if this arrangement of electrons were all that is required to produce paramagnetism, a considerable number of gases would be paramagnetic, whereas so far as is known only two possess this property. The consideration of the arrangement of the electrons in gaseous compounds shows, however, that the configuration of O_2 is almost unique in this respect. Consider the arrangement of electrons in some compounds of oxygen, *e.g.*, in water where it is in combination with two monovalent atoms, the electrons are arranged in an octet which has *two* sets of four electrons in parallel planes, if adjacent sets rotate in opposite directions, the total magnetic effect will be zero. The same is true for a compound like CaO, or for one like CO_2, where there are four such sets. We see that whenever the oxygen atom occurs, as it always does in valency compounds, with two additional electrons forming an octet, the effect of one face of the octet will always balance that of the other. In a neutral *atom* of oxygen the electrons would be arranged at the corners of an octahedron; if this were to rotate about one of its axes, the four electrons at right angles to the axis would form an unbalanced system and this would have magnetic properties. The magnetic properties of NO, if we take the arrangement of the electrons to be as that given in the first lecture, would arise from the rotation of the three electrons inside the octet, those on the octet itself would not contribute to the magnetic properties. In the compound C_2H_4 we have a similar arrangement of electrons to those in O_2, but in C_2H_4 all the massive positive charges are not as they are in O_2 on a straight line. The result of this is that if the two octets rotate, say about the line joining the two carbon atoms, they would either have to carry the hydrogen atoms with them, in which case the moment of inertia would be enormously

increased, or else move the electrons relative to the hydrogen atoms; the forces between the positive charges and the electrons would resist this motion, and tend to stop the rotation. In the oxygen molecule the electrons can rotate while the positive parts are at rest. If the compounds NCl or NF existed, the arrangement of the electrons would be as in O_2, and on the views we have been expressing we should expect that these compounds would be magnetic.

DIAMAGNETISM.

The diamagnetic properties of chemical compounds will furnish, I think, many searching tests of any theory of the distribution of electrons among the atoms of the compound. According to the theory of diamagnetism given by Langevin,[29] the contribution of an atom to k, the coefficient of diamagnetism, is equal to $\frac{1}{4}\frac{e^2}{m}\Sigma r^2$. Where $m\Sigma r^2$ represents the moment of inertia of the electrons in the atom about an axis through their centre of figure. The distribution of electrons is supposed to be quite symmetrical so that the moments about all axes are equal, e is the charge and m the mass of an electron.

If n is the number of atoms per unit volume, k, the coefficient of magnetization is given by the equation

$$k = \frac{1}{4} n \frac{e^2}{m} \Sigma r^2 \qquad (32)$$

If M is the molecular weight of the system, $\triangle$ the density of the substance, N the number of hydrogen atoms in a gram of hydrogen

$$n = \frac{\triangle}{M} N \qquad (33)$$

hence

$$\frac{kM}{\triangle} = \frac{1}{4}\frac{e^2}{m} N\Sigma r^2 \qquad (34)$$

Thus $kM/\triangle$, which is called the atomic diamagnetic coefficient and is denoted by χ_a, is proportional to Σr^2, and when χ is known Σr^2 can be calculated. We pass on to consider, what, for our purpose, is the most important application of diamagnetism—the connection between the diamagnetic coefficient of a compound, and those of its constituents.

Pascal[30] has made a series of most valuable experiments on this

[29] *Annales de Chimie et de Physique* [8], **5**, 70 (1905).
[30] *Annales de Chimie et de Physique* [8], **25**, p. 289.

point, chiefly on organic compounds. He finds that the connection between χ_m, the diamagnetic constant of a compound $A_xB_yC_z$ and χ_a, χ_b, χ_c, the constants for its constituents, is expressed by the relation

$$\chi_m = x\chi_a + y\chi_b + z\chi_c + \lambda. \qquad (35)$$

Where λ is a quantity, generally small compared with χ_a, χ_b, χ_c, which depends on the "bonding" of the atoms. Thus, for example, when oxygen is one of the constituents of the molecule, the value of λ, when the oxygen is connected by two linkages with a carbon atom, is not the same as when the oxygen is connected by one link with a carbon and by another to a hydrogen atom; thus, for example, the contributions of the two oxygen atoms in formic acid HCO.OH are different.

Pascal was dealing with valency compounds; in these, on the electron theory, the atom of any particular element will be associated with the same number of electrons whatever may be the compound in which it occurs; thus, for example, the electronegative elements O, S, F, Cl, will always be surrounded by an octet of electrons; the outer layers of the electropositive elements will have been transferred to the electronegative ones to make up their octets. An interesting point arises here in connection with the hydrogen atom and to a less extent with metal atoms. In a compound of hydrogen with an electronegative element, the electron associated with the hydrogen atom has gone to make up the octet round the negative ion, as, for example, in HCl. Thus the hydrogen atom in such a compound is but a positive core, it has no electrons associated with it, and hence on the electron theory of diamagnetism would not contribute anything to the diamagnetic coefficient. Pascal, however, in deducing the coefficient for any compound, assigns to hydrogen a constant value. This is to some extent a matter of bookkeeping, the electrons transferred from the hydrogen to the chlorine will increase the contribution of the chlorine atom to the diamagnetic coefficient. If we like we may transfer this increase to the credit of the hydrogen atom and regard the hydrogen atom as making a contribution to the diamagnetic coefficient, though it does this not by acting itself as the centre of one of the molecular currents, which account for diamagnetism, but by furnishing an electron which increases the molecular currents in some other atom. We should, however,

expect that the amount of the increase would depend upon the kind of atom to which the electron is transferred, that it would increase with the radius of this atom and thus be greater for bromine than for fluorine or chlorine.

We shall now consider what relation would be indicated on the theory we are considering between the diamagnetism of a compound and of its constituents. On the view that, at any rate, in valency compounds there is a transference of electrons from one atom to another, the atoms in the compound are not in the same state as when they were free and uncombined. The atoms of the electronegative elements such as oxygen or chlorine have gained electrons, while those of the electropositive elements have lost them. The coefficient of diamagnetism is proportional to the sum of the moments of inertia of the electrons about an axis through their centre of figure parallel to the magnetic force. If the transference of the electrons involves a change in this moment the coefficient of diamagnetism will be altered by chemical combination, *i.e.*, the additive law will not hold.

Suppose that in the free state the distances of the electrons from the centres of the atoms of the elements A and B are r_a and r_b, respectively, and that the electrons are symmetrically distributed. Then if there are α electrons on A, β on B the coefficient of diamagnetism is proportional to

$$\frac{2}{3}\alpha r_a^2 + \frac{2}{3}\beta r_b^2. \qquad (36)$$

If, as the result of chemical combination α atoms are transferred from A to B, if R_b is now the distance of the electrons on the B atoms from its centre the coefficient of diamagnetism is now

$$\frac{2}{3}(\alpha + \beta)R_b^2 \qquad (37)$$

This may be written in the form

$$\frac{2}{3}\alpha r_a^2 + \frac{2}{3}\beta r_b^2 + \frac{2}{3}\alpha\left(R_b^2 - r_a^2\right) + \frac{2}{3}\beta\left(R_b^2 - r_b^2\right) \qquad (38)$$

the sum of the first and second terms is the value given by the additive law, the remaining terms represent corrections which must be applied to obtain the diamagnetic coefficient of the compound. If χ_{AB} represents this coefficient, we see

$$\chi_{AB} = \chi_A + \chi_B + \alpha\lambda_{AB} + \frac{2}{3}\beta\left(R_b^2 - r_b^2\right) \qquad (39)$$

when $\lambda_{AB} = \frac{2}{3}(R_b^2 - r_a^2)$ and is a function which involves the

dimensions of each of the atoms at the ends of the bond binding them together. The term $\frac{2}{3}\beta^2(R_b^2 - r_b^2)$ depends only upon the atom B, hence the equation may be written as

$$\chi_{AB} = \chi_A + \chi'_B + \alpha\lambda_{AB} \qquad (40)$$

where χ'_B depends only upon the properties of the B atom.

Applying the same reasoning to the most general case, we see that χ the value for the compound $A_xB_yC_z$ will be given by an equation of the form $\chi = x\chi(A) + y\chi(B) + z\chi(C) + \Sigma\lambda_{AB}$.

A term has to be introduced into $\Sigma\lambda_{AB}$ for each electron transferred, *i.e.*, for each valency bond in the compound. Thus we may regard the diamagnetic coefficient of a compound as consisting of a series of terms, one set depending on the atoms in such a way that each atom contributes a definite amount depending only upon the atom; the second set of terms depending on the valency bonds, each bond contributing a term, the value of which depends upon the dimensions of the atoms at the ends of the bond. There may be a term in this set even when the atoms at the ends of the bond are the same; for example, when we have single or double bonds between two carbon atoms: For from the expression for λ we see that they would not vanish unless the radius of the octet round the carbon atoms in the compound C – C was equal to the distance of an electron in a free carbon atom from the centre. As the radius of the octet, round the carbon atoms when there is a double bond C = C is not the same as when there is only a single bond, the value of λ for a double bond is not necessarily twice that for a single one.

Pascal found that a double bond produced a very appreciable *diminution* in the diamagnetism, the magnitude of the effect of the double bond was about equal in magnitude, though opposite in sign to that due to a single carbon atom. The effect of a triple bond was much smaller than that of a double one.

Pascal's researches on the diamagnetism of compounds show that what we have called the λ terms are not in general large compared with the atomic ones, yet these terms undoubtedly exist. He shows, for example, that the contribution of oxygen to the diamagnetic coefficient is not the same, when as in CH_3OH the oxygen is linked by one bond to the carbon and by another to the hydrogen as it is in CH.O.OH, where one of the oxygen atoms is linked by two bonds to the carbon atom; he shows, too, that the

contributions of doubly and singly linked carbon atoms are different; he shows in fine that to calculate the diamagnetic coefficient of a compound we must take into account the constitution and configuration as well as the chemical composition.

In addition to the effects produced by the bonding of the atoms, there are others, though probably not so important, arising from what may be called the compressibility of the cell of electrons surrounding the atoms. Thus, for example, it is probable that the distance of the electrons from the centre of the chlorine atoms in HCl is not quite the same as in CCl_4, where the four chlorine atoms may compress each other by their mutual repulsions. A change in the dimensions of the atom would give rise to a change in the diamagnetic coefficient.

The corrections due to the λ terms amount in some cases to as much as 30 per cent., though it is exceptional for them to be as large as this.

From the equation

$$\chi_a = -\frac{1}{4}\frac{e^2}{m} N\Sigma r^2 \qquad (41)$$

we can, if we know the value of χ_a, deduce the distance of the electrons from the centre of the atom. For if the distribution of the electrons in the outer layer is symmetrical about the centre

$$\Sigma r^2 = \frac{2}{3} nR^2 \qquad (42)$$

where n is the number of electrons in the outer layer and R the distance of these from the centre of the atom; hence

$$\chi_a = -\frac{1}{6}\frac{e^2}{m} NnR^2 \qquad (43)$$

or since $e/m = 1.87 \times 10^7$; $e = 1.6 \times 10^{-20}$; $N = 6.16 \times 10^{23}$

$$\chi_a = -3.06 \times 10^{10} \times R^2 \times n. \qquad (44)$$

Pascal[31] gives the following values for $-10^6\ \chi_a$.

H	2.93	Al	13.2	As	43	Te	37.5
Li	4.20	Si	20.0	Sc	23	I	44.6
Bc	8.55	P	26.3	Br	30.5	Cs	41.0
B	7.30	S	15	Rb	27.2	Ba	38.2
C	6.80	Cl	20.1	Sr	24.5	An	45.8
N	5.57	K	18.5	Ag	31	Hg^{II}	33.4
O	4.61	Ca	15.0	Cd	20	Pt	40.3
F	5.95	Cu	18	In	15	Pb	45.8
Na	9.2	Lu	13.5	Sn^{IV}	30.3	Bi	192
Mg	10.1	Ga	16.8	Sb^{III}	74.0		

[31] *Comptes Rendus*, 158, p. 1895.

From these values of χ_a we find from the preceding equation the following values for the diameters of fully charged electronegative atoms. The values found by W. L. Bragg [32] are given for comparison.

Element.	Diameter from Diamagnetic Constant.	Values Found by Bragg.
O	1.02×10^{-8}	1.30×10^{-8}
F	1.05×10^{-8}	1.35×10^{-8}
S	1.84×10^{-8}	2.05×10^{-8}
Cl	2.0×10^{-8}	2.10×10^{-8}
Se	2.23×10^{-8}	2.35×10^{-8}
Br	2.40×10^{-8}	2.38×10^{-8}
Te	2.8×10^{-8}	2.66×10^{-8}
I	3.0×10^{-8}	2.80×10^{-8}

The agreement between the values of the diameters found from the diamagnetic coefficient and those found by Bragg is fairly close. It is interesting to note that there is nothing exceptional in the value of the strongly paramagnetic element oxygen, from this we conclude that the oxygen atom when it has two additional electrons is not paramagnetic.

When the diamagnetic substance is in a solid state a somewhat different treatment is required. If it is a metal, the electrons will be arranged in lattices and along these lattices the electrons may be free to move. If these lattices form a simple cubical system, then it can be shown that the effect of the electrons on the lattices in a plane at right angles to the magnetic force is to produce per unit area of this plane a magnetic moment equal to $-\frac{1}{16}\frac{He^2}{m}$, when H is the magnetic force, if d is the distance between two parallel lattice planes the moment due to the electrons in unit volume is $-\frac{1}{16}\frac{He^2}{md}$, hence the coefficient of diamagnetism is equal to $\frac{1}{16}\frac{e^2}{md}$.

Since the radius of an electron is of the order e^2/m, we see that the volume coefficient of diamagnetism is of the order of the ratio of the radius of the electron to the distance between adjacent atoms.

[32] *Phil. Mag.*, 40, p. 169.

Since the volume coefficient of diamagnetism varies as l/d, and the atomic volume varies as d^3, we see that for metals of the same valency the diamagnetic coefficient should vary inversely as the cube root of the atomic volume.

ELECTRON THEORY OF SOLIDS.

We shall now proceed to examine how atoms can be bound together not merely in twos or threes to form molecules, but in large numbers so as to form solids. We shall consider how such a collection of atoms is held together and calculate some of its physical properties. We begin with the case when the atoms are all of one kind and when the solid is a crystal, so that it may be regarded as made up of units which are repetitions of each other. These units will be built up of atoms and electrons and the proportion between the number of atoms and the number of electrons will depend upon the valency of the element. Thus for the alkali metals there will be as many atoms as electrons, for the alkaline earths there will be two electrons for each atom, for trivalent metals like aluminum there will be three electrons for each atom and so on. Since the units completely fill space, they must be of the shape of one of the solids into which space may be divided, *i.e.*, the units must be parallelipeda, hexagonal prisms, rhombic dodecahedra or cubo-octahedra.

Let us take the case where the units are cubical. When a number of cubes are built up into a solid each corner of a cube will be the meeting place of eight cubes. Thus, if for purposes of calculation, we take the cube as our unit, and proceed to find the effect of one cube and take the sum of these effects for all the cubes into which the solid is divided, the effect due to an atom or electron at a corner will be counted eight times over. We may compensate for this by assigning to an atom or electron at the corner one-eighth of its normal charge. An atom or electron at the centre of the face of a cube would be common to two cubes and so must be assigned half its normal charge, while an atom or electron at the middle point of a side of a cube will form a part of four cubes and so must be given one-quarter the normal charge.

Thus suppose the atom is at the centre of a cubical layer of electrons, then if the electrons are at the corners of the cube,

both electrons and atoms will be arranged in simple cubical lattices, there will be as many electrons as atoms, the unit cell will be a cube with one-eighth of an electron at each corner and an atom at its centre. Suppose the electrons are at the middle points of the faces of the cube as well as at the corners, there will be four electrons for each atom so that the arrangement will be a possible one for a quadrivalent element. The symmetry of the arrangement shows that it corresponds to a crystal in the regular system. The cell in this case will be a cube with one-eighth of an electron at each corner and half an electron at the centre of each face.

Another quite symmetrical arrangement is when there is an electron at the corner of each cube and one at the middle point of each of its twelve sides; as each side is shared by four cubes the twelve electrons at the middle of the sides will only furnish three electrons to the cell, the one-eighth of an electron at each of the corners will contribute another, so that this arrangement would again be representative of an element in which there are four electrons per atom. The cell in this case will be a cube with one-eighth of an electron at each corner, one-quarter of an electron at the middle point of each side and an atom with a charge four at the centre.

The arrangement of the atoms in each of the preceding cases is that of a simple cubical lattice, the experiments of Sir William and Prof. W. L. Bragg on crystal structures have shown that one of the most frequent arrangements of the atoms is that of face-centred cubes. Here the atoms are at the corners and the centres of the faces of the cubes. If such a cube is taken as the unit cell, one-eighth of an atom must be placed at each corner and half an atom at the centre of each face: This makes each cell contain four atoms. If the atom is one of a monovalent element like lithium, the cell must contain four electrons. These electrons can be arranged with cubical symmetry in two ways—

1. By putting one-quarter of an electron at the middle point of each edge and one at the centre of the cube. This gives an arrangement where each atom has six electrons and each electron six atoms for its nearest neighbours. The atoms and electrons are arranged alternately at equal intervals along the lines of a simple cubical lattice.

This arrangement corresponds to that formed by Sir William and Prof. W. L. Bragg for the chlorides of the alkali metals.

2. Put one electron at the centre of four out of the eight cubes into which the unit cube is divided by planes bisecting the sides at right angles. The four cubes are to be chosen as follows: Take any one and put an electron at its centre, then electrons are to be put at the centres of the three cubes which have an edge but not a face in common with the cube originally chosen. When the cells are put together the same rule must be observed, any two small cubes which have a face in common must have an electron at the centre of one but not at the centre of the other. The four electrons in each cell are at the corners of a regular tetrahedron. The distribution of the atoms and electrons is equivalent to one where each atom is at the centre of a regular tetrahedron of electrons and each electron at the centre of a regular tetrahedron of atoms.

DIVALENT ELEMENTS.

If the atoms in the face-centred cell belong to a divalent element, since there are four atoms in the cell there must be eight electrons.

Two ways in which this may be done are as follows:

1. Fill up the four small cubes which were left empty on scheme 2 for the monovalent elements. Each atom will now have eight electrons as its nearest neighbours, the electrons being at the corners of a cube with the atom at its centre. The cubes surrounding two adjacent atoms have an edge in common and not a face as in the simple cubical arrangement for monovalent atoms.

2. Take the scheme 2 for four of the electrons and in addition place a quarter of an electron at the middle point of each of the twelve sides of the large cube and another electron at its centre.

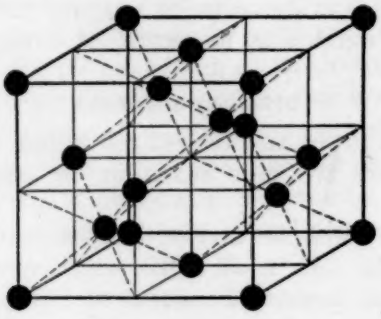
TRIVALENT ATOMS.

When the atoms in the face-centred cube are trivalent there must be twelve electrons in the unit. We can find accommodation for these if we put one at the centre of each of eight small cubes into which the unit cube is divided, a quarter of one at the middle points of each of the twelve edges of the unit cube and another at the centre of this cube. This arrangement is equivalent to putting the atoms at the centres and the electrons at the corners of a series of rhombic dodecahedra filling space.

TETRAVALENT ELEMENT.

The arrangement of the atoms in the diamond has been worked out by the Braggs. It is that shown in Fig. 40. The unit contains eight atoms distributed as follows: One-eighth at each of the corners of the unit, this accounts for one; one-half at the centre of each of the faces, this accounts for three; and four more at the centres of four of the eight cubes into which the unit cube is divided by planes bisecting the sides at right angles. The cubes to be occupied by the atoms are chosen by the same rule as that given for the arrangement of the electrons for the centre-faced arrangement for the monovalent element. As the unit

FIG. 40.



contains eight carbon atoms and carbon is quadrivalent, there must be thirty-two electrons in the unit; these may be arranged as follows:

(*a*) At the middle points of the sides of the cubical unit; this accounts for three.

(*b*) At the centre of each of the faces of the eight small cubes; this accounts for twenty-four.

(*c*) At the centres of the four small cubes not occupied by the carbon atoms; this accounts for four.

(*d*) One at the centre of the large cube.

Röntgen-ray analysis has shown that for some elements the atoms are arranged at the corners and the centre of a cube. Taking this cube as the unit it contains two atoms; if the element is monovalent, it must contain two electrons. We cannot place these electrons so as to get complete cubical symmetry for one such unit; if, however, we group eight such units together, we get a larger

cubical unit containing sixteen atoms, and it is possible to arrange sixteen electrons in this larger unit so as to get cubical symmetry. Thus we might put pairs of electrons along the diagonals of the eight cubes which go to make up the larger unit.

If the atom were a divalent one we should have to accommodate four electrons in the original unit. This may be done by putting them at the centres of four out of the eight cubes into which the unit may be divided.

HEXAGONAL SYSTEM.

We have hitherto confined ourselves to the consideration of crystals in which the unit was a cube and the arrangement both of atoms and electrons completely symmetrical, so that the crystals would belong to the regular system. If our unit were a hexagonal prism, if, for instance, the electrons were at the corners and the atoms at the centres of hexagonal prisms, then since each corner is common to six prisms, we must, when calculating the electrical forces due to the unit, give to each electron at the corner one-sixth of its normal charge, the twelve electrons at the corners are thus equivalent to two electrons, so that the unit contains two electrons for each atom and would thus correspond to a divalent element.

The arrangement of electrons and atoms in the systems we have described have such regularity that the calculation of the properties of such an aggregate is easier than that of the properties of an aggregate of a small number of atoms in an individual molecule. For the electrons in one part of a molecule, for example, those at the ends of the two octets which form the oxygen molecule, are exposed to forces which are different from those acting on the electrons between the two oxygen atoms. The greater regularity in the arrangement of the electrons in the crystal more than compensates, as far as the mathematical difficulties are concerned, for the necessity of taking into account the effect of a much larger number of electrons and atoms than is necessary for the molecule.

I have in a paper published in the *Philosophical Magazine* (**53**, p. 721) calculated some of the properties of crystals when the atoms and electrons are arranged according to some of the schemes we have just been discussing. I shall describe the results of these investigations, beginning with the simplest case,

where the atoms and electrons are both arranged in simple cubical lattices, where each atom may be regarded as the centre of a cube formed by eight electrons.

In the paper referred to, the stability of the system is investigated, and it is shown that if $2d$ is the distance between two atoms the arrangement will be stable, provided d is less than $c/1.69$ where c is the distance at which the force exerted by the positive nucleus on an electron changes from attraction to repulsion. As the distance between an atom and the nearest electron is $\sqrt{3}d$, *i.e.*, $1.72d$, we see that for the equilibrium to be stable, the shortest distance between an atom and an electron in the solid cannot exceed by more than a very small amount the distance of the electron from the centre of the atom when the element is in the gaseous state.

The system of electrons and atoms in the metal will have a very large number of periods of vibration, depending on the way the electrons are displaced relatively to each other and to the atoms; the highest frequency of these vibrations is when the electrons are not displaced relatively to each other, but only with respect to the atoms; this corresponds to the displacement which would be produced by light whose wave-length is long compared with the distance between two atoms. I find that this maximum frequency, p, is given by the equation

$$mp^2 = .384\, ce^2/d^4 \qquad (45)$$

where m is the mass and e the charge on an electron.

If M is the mass of an atom and $\triangle$ the density of the solid, then since $8d^3$ is the volume of a cell, $1/8d^3$ is the number of cells in a cubic centimetre, hence

$$\frac{M}{8d^3} = \triangle \qquad (46)$$

so that equation (45) may be written as

$$mp^2 = .384\, e^2 \frac{8\triangle}{M} \frac{c}{d} \qquad (47)$$

This type of vibration is the one that would be excited by waves such as those of visible or ultra-violet light whose wave-length is large compared with the distance between the atoms in the solid. We might therefore expect evidence of it in the behaviour of monovalent metals when acted upon by light, the effect produced upon such metals would be greatest when the frequency of the incident light was that given by equation (45).

An interesting case when the action of light on a metal is a maximum for light of a particular wave-length is what is known as the selective photoelectric effect.[33] This has been measured by Pohl and Pringsheim,[34] and in the following table, I give the comparison of the wave-length λ for which the selective photoelectric effect is a maximum for the monovalent metals sodium, potassium and rubidium as determined by Pohl and Pringsheim with the wave-lengths calculated by equation (45) where c/d has been given the value 1.7, *i.e.*, on the supposition that the shortest distance between the atom and the electron in the metal is the same as that in the gas.

Metal.	Δ	$M/1.64 \times 10^{-24}$	λ calculated.	λ observed.
Sodium	.971	23	3234	3400
Potassium	.862	39	4457	4400
Rubidium	1.532	85.45	4940	4800

It will be noticed that the agreement between the observed and calculated values is satisfactory.

It is interesting to compare the frequency of this type of vibration of the electrons in the solid, with P, that of the vibration of the electron in a gaseous atom, the latter can easily be proved to be given by the equation

$$mP^2 = e^2/c^3 \qquad (48)$$

so we see from (1) if $1.7d = c$ and p is the frequency in the metal

$$p = 1.8P \qquad (49)$$

thus the frequency in the metal is a little less than twice that in the gas, the values for the wave-length of the vibrations in the gaseous atom deduced from the table just given are for sodium 5800, and for potassium 7900.

The slowest vibrations of the electrons are when the displacement of adjacent electrons are in opposite directions. Thus suppose one of the lines of the electron lattice is vertical, then the slowest vibration of the electrons is when the electrons in any one line have all equal vertical displacements and the displacements of the electrons in the six vertical lines which are its nearest neighbours are equal in magnitude, but opposite in direction, to that in the line under consideration.

[33] Hughes, "Photoelectricity," Chap. 5.

[34] *Verh. d. Deutsch. Phys. Gesell.*, **13**, p. 474 (1911).

COMPRESSIBILITY OF THE METALS.

We can calculate the potential energy due to the forces between the atoms and the electrons. I have given the calculations in a paper in the *Philosophical Magazine* (**43**, p. 721) and have shown that if the metal is supposed to be made up of cubical cells with an atom at the centre and one-eighth of an electron at each of its eight corners, each cell corresponding to an atom with its electron, the potential energy per cell is

$$-1.825\frac{e^2}{2d} \tag{50}$$

when $2d$ is a side of the cube. Thus, if there are N cells per unit volume, the potential energy per unit volume is

$$-1.825\frac{e^2}{2d}N \tag{51}$$

Now $N = 1/8d^3$, and if as before M is the mass of an atom and $\triangle$ the density of the metal

$$NM = \triangle \tag{52}$$

hence the potential energy per unit volume is equal to

$$-1.825\,e^2\left(\frac{\triangle}{M}\right)^{\frac{1}{3}} \tag{53}$$

It is shown also that the work required to compress the cells so that the distance between two atoms is reduced from $2d$ to $2(d-\triangle d)$ is equal to

$$1.825\frac{Ne^2}{2d}\left(\frac{\triangle d}{d}\right)^2 \tag{54}$$

If dV is the diminution in a volume V due to this diminution in d

$$\frac{dV}{V} = 3\frac{\triangle d}{d} \tag{55}$$

hence the work required to compress the cells in unit volume is equal to

$$\begin{aligned}&\frac{1.825}{9}\frac{N}{2d}e^2\left(\frac{dV}{V}\right)^2\\ &=\frac{1.825}{9}e^2\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}\left(\frac{dV}{V}\right)^2\end{aligned} \tag{56}$$

But if k is the bulk modulus, then this work is equal to

$$\frac{1}{2}k\left(\frac{dV}{V}\right)^2 \tag{57}$$

hence

$$k = \frac{3.65}{9}e^2\left(\frac{\triangle}{M}\right)^{\frac{1}{3}} \tag{58}$$

The "compressibility" of the substance is equal to $1/k$.

We owe to Professor Richards invaluable determinations of the compressibility of the various elements. The following table contains the results of the comparison of his values of the compressibility with those calculated from equation (58).

Metal.	Δ	$M/1.64 \times 10^{-24}$.	k calculated.	k observed.
Lithium	.534	7	$.14 \times 10^{12}$	$.114 \times 10^{12}$
Sodium	.971	23	$.068 \times 10^{12}$	$.065 \times 10^{12}$
Potassium	.862	37	$.03 \times 10^{12}$	$.032 \times 10^{12}$
Rubidium	1.532	85.5	$.022 \times 10^{12}$	$.025 \times 10^{12}$
Cæsium	1.87	132	$.016 \times 10^{12}$	$.016 \times 10^{12}$

Thus the results given by equation (58) are in close agreement with experiment.

If the atoms are in the gaseous state, the work required to change the radius of an atom from r to $r - \Delta r$ is equal to $\frac{1}{2}\frac{e^2}{c}\left(\frac{\Delta r}{r}\right)^2$. Thus to produce the same percentage changes (45) in the sum of the volume of the atoms when in the gaseous state and (47) in the volume of the same number of atoms in the solid state requires the expenditure of amounts of work which are in the proportion of $\frac{1}{c}$ to $\frac{1.825}{d}$, or if $1.7d = c$, of 1 to 3.●. Thus the compressibility of the atoms in the solid state is about one-third of that in the gaseous.

The potential energy of a cell in the solid is equal to $\frac{-1.825e^2}{2d}$ or, since $\frac{1}{(2d)^3} = \Delta/M$, to $-e^2\ 1.825\left(\frac{\Delta}{M}\right)^{\frac{1}{3}}$; if M' is the atomic weight of the element

$$M = 1.64 \times 10^{-24} \times M' \tag{59}$$

hence the potential energy of the metal per cell is equal to

$$-e^2\ 1.5 \times 10^8 \left(\frac{\Delta}{M'}\right)^{\frac{1}{3}} \tag{60}$$

This is equal to the energy acquired by the charge on an electron falling through a potential difference of

$$21.25 \times \left(\frac{\Delta}{M'}\right)^{\frac{1}{3}} \text{ volts.} \tag{61}$$

The values for the various alkaline metals are

Li = 9.25 volts
Na = 7.3
K = 6.36
Rb = 5.52
Cs = 5.100

The work which must be done to pull the cell from the metal and convert it into an atom of a monatomic gas is the difference between the potential energy in the cell and the potential energy of the gaseous atom; the latter when expressed in volts is for a monovalent element equal to the ionising potential.

The potential energy per cell is equal to $-\frac{1}{2}(w_1 + w_2)$ where w_1 is the work required to remove a single electron from the metal and w_2 that required to remove a single atom. We have calculated $w_1 + w_2$, but not w_1 and w_2 individually. If the repulsion between the positive parts of two atoms was proportional to the inverse square of the distance, then w_1 would be equal to w_2, but if the repulsion is equal to $\frac{e^2}{r^2}\left(1 - \frac{c\rho}{r}\right)$, then w_2 will be greater than w_1, and w_1 will be less than $\frac{1}{2}(w_1 + w_2)$. Let $w_1 = \frac{\beta}{2}(w_1 + w_2)$ where β is a fraction, then the work required to remove any electron from the alkali metals will be β times the values given in the preceding tables. The contact difference of potential between two metals is equal to the difference in the amounts of work required to remove an electron from the two metals, thus the contact difference of potential between sodium and potassium would be $\beta\ (7.3 - 6.36) = .92\ \beta$ volts. The value found by experiment is .4 volt, hence $\beta = .44$, so that $w_1 = .44$ (potential energy per cell).

This gives the following values for the work required to tear an electron from the alkali metals.

Lc	= 4.07 volts
Na	= 3.2
K	= 2.79
Rb	= 2.42
Cs	= 2.24

The work required to tear an electron from sodium was estimated by Richardson from thermionic data as 2.6 volts, and from the photoelectric effect as 2.1 volts. The values given in the table represent the work required to remove an electron from the *body* of the metal; the atoms in the surface layers of the metal differ in energy from those in the interior, and an electron can escape from them with less expenditure of energy. As the values given in the table are less than half the amount of work required to remove both an electron and the positive part of an atom from the

metal, the work required to remove an atom is greater than that required to remove an electron, so that when the metal is heated, the number of positive ions which come off will be small compared with the number of electrons.

The values given on page 161 for the compressibility are for a distribution of atoms and electrons such that the atoms are at the centres of cubes and the electrons at the corners.

When the atoms and electrons are arranged so that atoms and electrons occur alternately at equal intervals along the lines of a cubical lattice, we can show that the electrostatic potential energy for a volume of the metal containing N electrons and N atoms is

$$-1.77\frac{Ne^2}{d} \tag{62}$$

where d is the shortest distance between an atom and an electron. If these N atoms and electrons make up unit volume, then if $\triangle$ is the density of the metal and M the mass of an atom, since a cube with side $2d$ contains four atoms

$$\begin{gathered}\frac{4M}{8d^3} = \triangle: \quad NM = \triangle \\ \frac{1}{d} = \left(\frac{2\triangle}{M}\right)^{\frac{1}{3}}\end{gathered} \tag{63}$$

hence the electrostatic energy per unit volume is

$$\begin{aligned}&-1.77\,e^2 2\,\frac{1}{3}\left(\frac{\triangle}{M}\right)^{\frac{1}{3}} \\ &= -2.2e^2\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}\end{aligned} \tag{64}$$

It follows from this that the bulk modulus is

$$\frac{2.2e^2}{9}\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}, \tag{65}$$

this is not very much more than half the value $\frac{3.65\,e^2}{9}\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}$ corresponding to the other distribution which we saw agreed very well with the experiment results; hence we conclude that the atoms and electrons cannot in the alkali metal be arranged so as to occur alternately at equal intervals along the lines of a cubical lattice.

For the arrangement where the atoms are arranged in face-centred cubes with electrons at the centres of four out of the eight smaller cubes into which the face-centred cube is divided, I

find that the electrostatic potential energy for a volume containing N atoms and N electrons is

$$-3{\cdot}50\left(\frac{\Delta}{M}\right)^{\frac{1}{3}} \tag{66}$$

so that k, the bulk modulus, is equal to

$$\frac{-3{\cdot}50}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{1}{3}} \tag{67}$$

this differs by less than 5 per cent. from the value given by equation (58), and would agree within the errors of experiments with the values found by Richards.

When the arrangement of the atoms of a monovalent element is that of the body-centred cube and the electrons are placed two by two along the diagonals of eight such cubes taken as a single unit, Miss Woodward finds

$$k = \frac{3{\cdot}2}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{1}{3}} \tag{68}$$

This would give values for k appreciably smaller than those found by experiment. The arrangement of the electrons was assumed to be as follows: Two electrons were placed inside each cube on a diagonal, one on one side of the centre, the other on the other, midway between the centre of the cube and the ends of the diagonal. The diagonals along which the electrons are placed are chosen so that in a cube built up of eight such small cubes no two of the diagonals in any four whose centres are in one plane are parallel or intersect. The diagonals in two cubes which have a corner but neither an edge nor a face in common are to be parallel. This arrangement is equivalent to arranging the atoms and electrons alternately at equal intervals along lines whose directions are parallel to the four diagonals of the cube.

THE ENERGY AND COMPRESSIBILITY OF DIVALENT ELEMENTS.

We shall further test the electron theory of solids by calculating the compressibility of a divalent element. Calcium crystallises in the regular system and the arrangement of the atoms has been shown by X-ray analysis to be that of the face-centred cube. Taking such a cube as the unit, it contains four calcium atoms; since calcium is divalent, if there are four atoms there must be eight electrons. The most symmetrical way of arranging these is to place one at the centre of each of the eight small cubes into which the unit cube is divided by planes bisecting its sides at right angles.

Taking this arrangement, I find that the electrostatic potential energy of a calcium atom is, if $2d$ is a side of the unit cube,

$$-\frac{e^2}{d}\,5.33 \tag{69}$$

while that of an electron is equal to

$$-\frac{e^2}{d}\,1.8 \tag{70}$$

Hence the electrostatic potential energy of one atom and two electrons is

$$-\frac{e^2}{d}\,8.93 \tag{71}$$

The total actual potential energy, *i.e.*, the potential energy when we take into account the effect of the forces varying inversely as the cube of the distance is one-half of this, *i.e.*,

$$-\frac{e^2}{d}\,4.46 \tag{72}$$

Since the cube whose volume is $8d^3$ contains four atoms

$$\frac{4M}{8d^3} = \triangle \tag{73}$$

where M is the mass of an atom and $\triangle$ the density of the metal; hence the energy per unit volume is equal to

$$-e^2\,5.61 \times \left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \tag{74}$$

The bulk modulus k is equal to

$$e^2\,\frac{11.2}{9}\left(\frac{\triangle}{M}\right)^{\frac{4}{3}} \tag{75}$$

for calcium $\triangle = 1.55$ and $M = 40 \times 1.64 \times 10^{-24}$, hence k for calcium $= .192 \times 10^{12}$. The compressibility which is the reciprocal of k is 5.2×10^{-12}; the value found by Richards is 5.5×10^{-12}, so that the agreement between the observed and calculated values is quite satisfactory.

The potential energy for an atom and two electrons is that corresponding to the fall of an electron through twenty-two volts.

THE COMPRESSIBILITY OF A TRIVALENT ELEMENT.

Aluminum is a trivalent element crystallising in the regular system. The arrangement of the atom has been shown to be that of a face-centred cube. Taking this cube as the unit it contains four atoms; it must, therefore, since aluminum is trivalent, contain twelve electrons. If we place electrons at the middle points of the sides, at the centres of each of the eight cubes into which the unit cube is divided by bisecting planes and one at the centre of the

cube, we get a symmetrical distribution of these twelve electrons. This distribution is the same as if each atom were placed at the centre of a rhombic dodecahedron and the electrons at the corners of the dodecahedron. Since four planes meet at some of the corners while only three meet at others, we see that the electrons will be divided into two groups.

For this arrangement I find that the electrostatic potential energy of the atom, with its triple charge of electricity, is equal to

$$-e^2\frac{10.6}{d} \tag{76}$$

where $2d$ is the side of the face-centred cube and e the charge on an electron.

For an electron at a corner of the dodecahedron where four planes meet, the potential energy is

$$-e^2\frac{05}{d} \tag{77}$$

and for an electron at a corner where three planes meet

$$-e^2\frac{1.75}{d} \tag{78}$$

Each atom is associated with one electron of the first type and two of the second, hence the electrostatic potential energy of this system is $-e^2\frac{14.25}{d}$ and the total potential energy $-e^2\frac{7.12}{d}$.

Now

$$\frac{1}{d}=\left(\frac{2\Delta}{M}\right)^{\frac{1}{3}} \tag{79}$$

hence k the bulk modulus is given by the equation

$$k=\frac{17.8}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}} \tag{80}$$

for aluminum $\Delta=2.65$, $M=27\times1.64\times10^{-24}$; hence $k=1.08\times10^{12}$, the value found by experiment is $.78\times10^{12}$.

COMPRESSIBILITY OF THE DIAMOND.

In the diamond we have a quadrivalent element crystallising in the regular system. The arrangement of the carbon atoms in the diamond has been shown by Sir W. H. Bragg and Prof. W. L. Bragg to be given by the following scheme. The atoms occupy

(*a*) the corners of a cube;

(*b*) the centres of its faces;

(*c*) four of the centres of the eight cubes into which the large cube is divided by planes bisecting its sides at right angles.

We shall take this cube as our unit; it contains eight carbon

atoms. Since carbon is quadrivalent, it must contain thirty-two electrons; these electrons will be situated

(*a*) at the middle points of the edges of the cubical unit; this accounts for three;

(*b*) at the centres of each of the faces of the eight small cubes; this accounts for twenty-four;

(*c*) at the centres of the four small cubes not occupied by the carbon atoms; this accounts for four;

(*d*) one at the centre of the large cube.

Making use of this unit, we can calculate the electrostatic potential energy due to the charges on the atoms and electrons. Let E be the charge on a carbon atom, e that on an electron.

The electrostatic potential energy of a carbon atom

$$\frac{1}{2}E\left(\frac{\Sigma e}{r'}-\frac{\Sigma E}{r}\right) \tag{81}$$

I find to be equal to

$$\frac{1}{2}\frac{E}{d}(149.346e-35.13E), \tag{82}$$

where $2d$ is the side of a unit cube. Since $E=4e$, this reduces to

$$17.65\frac{e^2}{d}. \tag{83}$$

The electrostatic potential energy of an electron I find to be

$$\begin{aligned}\frac{1}{2}\frac{e}{d}\left\{\frac{E}{4}\ 149.346-147.59e\right\}\\ =\frac{1}{2}\frac{e^2}{d}1.75.\end{aligned} \tag{84}$$

Hence the electrostatic potential energy for the atom and its four associated electrons is $21.15\ \frac{e^2}{d}$.

Since there are eight atoms in the cube whose edge is $2d$, if $\triangle$ is the density of the diamond and M the mass of a carbon atom,

$$\frac{8M}{8d^3}=\triangle \tag{85}$$

or

$$\frac{1}{d}=\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}. \tag{86}$$

Thus the electrostatic potential energy per one atom and four electrons is

$$21.15e^2\left(\frac{\triangle}{M}\right)^{\frac{1}{3}}, \tag{87}$$

and the energy per unit volume is

$$21.15e^2\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}. \tag{88}$$

Hence k, the bulk modulus of the diamond, is given by the equation

$$k = \frac{21.15}{9} e^2 \left(\frac{\Delta}{M}\right)^{\frac{1}{3}}; \qquad (89)$$

for the diamond $\Delta = 3.52$, $M = 12 \times 1.64 \times 10^{-24}$; hence $k = 5.6 \times 10^{12}$, $1/k = .178 \times 10^{-12}$.

This value for $1/k$ is much less than that, $.5 \times 10^{-12}$, found by Richards. It is, however, in close agreement with $.16 \times 10^{-12}$, the value recently found by Adams.[35]

The properties of solids formed by elements whose atoms have more than four disposable electrons are quite different from those of solids formed by the elements with one, two, or three disposable electrons. The latter are, with the exception of boron, metallic and good conductors of electricity and heat. The former, for instance sulphur and phosphorus, are insulators. Not only do they insulate in the solid state, but they do so after they are fused. They differ in this respect from solid salts which, though they may insulate when in the solid state, generally conduct when melted. This suggests that in the salts there are positively and negatively electrified systems which are fixed when the substance is in the solid state, but can move about when it is liquefied. In such elements as sulphur or phosphorus there does not seem to be any evidence of the existence of anything but neutral systems; in other words, the solid may be regarded as built up of units, each of which contains as much positive as negative electricity. It is noteworthy that according to the Electron Theory of Chemical Combination, two similar atoms, if they have each more than four disposable electrons, like the atoms of sulphur and phosphorus, can combine and form a saturated molecule, which is electrically neutral.

Thus we are led to distinguish three types of solids:

(*a*) A type where the atoms are arranged in lattices, and the electrons in other lattices coördinated with the atomic ones. In this type each electron has no closer connection with a particular atom than it has with several others. Thus, for example, when the electrons form a simple cubical lattice with the atoms at the centres of the cubes, each electron has eight atoms as equally near neighbours; so that an electron is not bound to a particular atom.

[35] *Washington Acad. Sc.*, 11, p. 45 (1921).

This type includes the metals; it also includes boron and carbon in the form of diamond, which are insulators.

(*b*) A type represented by the salts; here the atoms are again arranged in lattices, but each electron has much closer relation with one particular atom than it has with any other. Thus to take the case of NaCl, where the Braggs have shown the atoms to be arranged according to the following scheme:

Na Cl Na Cl
Cl Na Cl Na
Na Cl Na Cl

We suppose that each sodium atom has lost an electron, while each chlorine atom has gained one; thus each chlorine atom has eight electrons around it, and each electron is much more closely bound to one particular chlorine atom than to any other. It is so closely associated that it is not dissociated from its partner in either the solid or liquid state of the substance. Thus the chlorine system always has a negative charge, the sodium one a positive. These atoms do not move when the substance is in a solid state, though they may do so when it is liquefied.

If the distance of the electrons from the chlorine atoms were to increase until it was not far from half the distance between the sodium and chlorine nuclei, this type would approximate to type (*a*).

(*c*) A type where the lattices are built up of units which are not electrified; such units are probably molecules containing two or more atoms, though in certain cases they may be single atoms. The characteristic of the type is that each unit has sufficient electrons bound to it to make it electrically neutral, and that each electron remains attached to a particular atom. Thus where an electric force acts on the system there is no tendency to make the unit move in one direction rather than the opposite, so that the substance cannot conduct electricity.

There is something anomalous about the compressibility of silicon; the arrangement of its atoms as determined by X-ray analysis is the same as that of the diamond, while its atomic volume is 2.7 times greater. We might therefore expect that its compressibility would be (2.7), or 3.8 times that of the diamond. Its compressibility, however, as determined by Richards, is only $.16 \times 10^{12}$, which is practically the same as the revised value for

the diamond. In silicon, however, there are two layers of electrons so that when the four electrons in the outer layer have been distributed to form the lattice, a layer of eight will remain surrounding the positive part of the atom. The compression of the silicon may involve not merely the closer approach of the positive parts of the silicon atoms, but also a closer approach to the central

TABLE VIII.

Potential Energy per Atom with Its Associated Electrons.

Arrangement of Atoms.	K. (Bulk Modulus).
Monovalent Elements.	
CUBICAL	$\frac{3.65\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
FACE-CENTRED CUBE:	
Electrons at middle points of edges and centre of cube	$\frac{2.2\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Electrons at centres of four constituent cubes	$\frac{3.5\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
BODY-CENTRED CUBE	$\frac{3.2e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Divalent Elements.	
FACE-CENTRED CUBE:	
Electrons at centres of eight constituent cubes	$\frac{11.2\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Electrons at centres of edges and four constituent cubes	$\frac{7.75\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Trivalent Elements.	
FACE-CENTRED CUBE:	
Electrons at middle points of edges and centre of cube and at centres of four constituent cubes	$\frac{18\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$
Quadrivalent Elements.	
FACE-CENTRED CUBE and at:	
Centres of four constituent cubes. Electrons, centres of edges, centres of faces of constituent cubes and at centres of four of these cubes	$\frac{21.15\,e^2}{9}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$

atom of the layer of eight electrons which surround it. The work required to do this would tend to make the compressibility less than for a substance like carbon, which, after its outer layer has been distributed, has no inner layer left to compress.

The case may be compared with that of a chloride of an alkali metal, say LiCl. In the lattice formed by the atoms each chlorine atom is surrounded by a layer of eight electrons. The compressibility of the salt has been determined by Richards and it is much less than the value calculated on the supposition that the chlorine

ion with its octet of electrons round a positive charge of seven units can be treated as a negative charge of one unit at the centre of the chlorine atom. The compression of the octet round the chlorine atom has also to be taken into account. Miss Woodward has done this recently and finds that the calculated values are in fair agreement with those determined by experiment.

A similar argument applies to the elements copper, silver and gold, which are far less compressible after allowing for the difference in the atomic volume than they would be if they followed the same law as the other monovalent elements, the alkali metals. The heavier alkali metals have also inner layers, but the atomic volume of these is so great that the compression of these layers does not come nearly so much into play as in gold and silver, which have much smaller atomic volumes.

We may sum up the results of the preceding investigation of the compressibility of solids as follows:

The compressibility is equal to $C\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$, where C is a quantity depending on the valency of the element and the form in which it crystallises; Δ is the density of the solid and M the mass of an atom of the element.

The potential energy of an atom with its associated electrons is equal to

$$-\frac{4.5}{C}\left(\frac{\Delta}{M}\right)^{\frac{1}{3}} \qquad (90)$$

Table VIII contains a summary of the preceding results.

SURFACE TENSION.

The preceding expression represents the energy of an atom in the mass of the metal, for one on the surface it requires modification. Thus if P is an atom or electron part of its potential energy depends on the atoms and electrons above a horizontal plane through P. If the metal is broken so that this plane becomes a surface of the metal, the atoms and electrons above P will no longer affect the potential energy so that this will be changed. We can find an approximation to the amount of this change in the following way: Let us take a crystal of a monovalent element and suppose that the atoms and electrons are arranged in the plane of the surface according to the scheme when the atoms are at the corners and centres of the faces of a cube and the electrons at the middle points of the sides and the centre of the cube. This is the

more convenient arrangement to take, since the atoms are present in equal numbers in the plane, so that the total electric charge upon it is zero. With this arrangement I find that the contribution of the atoms and electrons above P to the potential energy of the system consisting of P and an electron is $-.075\frac{e^2}{d}$, where d is the distance between an atom and the nearest electron. We saw that in this case for an atom and electron in the interior the energy is $-1.77\frac{e^2}{d}$. Thus the potential energy S of the atom and electron in the surfaces exceeds I, the potential energy in the interior, by $\frac{.075}{1.77} I = .042\, I$. The surface tension arises from the excess of the potential energy of the atoms in the surface over those in the interior and is equal to the excess for one atom multiplied by the number of atoms in unit area of the surface. Let us apply this to find the surface tension of sodium. The energy of an atom of sodium not on the surface is equal to that gained by an electron falling through 7.2 volts, *i.e.*, $7.2 \times 1.6 \times 10^{-12}$ ergs. The distance between two sodium atoms is equal to 3.37×10^{-8}, hence the number of sodium atoms per square centimetre is $10^{16}/11.35$. Thus the surface tension of sodium is

$$.042 \times 7.2 \times 1.6 \times 10^4/11.35 = 432 \text{ ergs/cm.}^2 \qquad (91)$$

The value given in the tables for molten sodium is 500, so that the calculated and the observed value are of the same order of magnitude. The calculation is only a rough approximation as we have neglected the effect of temperature and supposed that the distance between the sodium atoms is the same on the surface as in the interior. The increase in the potential energy at a surface will depend upon the orientation of the surface. Thus if the face of the sodium is a plane parallel to the diagonal plane of the cube instead of the plane parallel to one of its faces, I find that the potential energy of an atom and electron at the surface will be greater than if they were in the interior by .067 I instead of .0423 I as in the former case. In this plane the number of atoms per unit area is only $1/\sqrt{2}$ that in the former case, thus the surface tension in this plane will be to that in a plane parallel to a face of the cube in the proportion of 47.3 to 42. The atoms in this plane having greater potential energy than those in a plane parallel to the faces of the cube will

develop a greater amount of heat when they enter into chemical combination. I find that for a gram molecule of sodium the difference would be about 10,000 calories. Thus chemical action would be more likely to go on at these faces than at the natural cleavage faces of the crystal; the photoelectric emission of electrons would also be greater.

COMMUNICATION OF A CHARGE FROM GASEOUS IONS TO THE ELECTRODES.

The preceding values have an important bearing on the transmission of electric charges from gaseous ions to metallic electrodes.

Consider first the case of a positively charged ion. If this is to give up the charge to the electrode and escape as an uncharged atom or molecule, an electron must come from the metal, and be received by the ion. Let the work required to abstract the electron from the metal be V_m and let the ionising potential of the gas be V_g, there the work required to discharge the ion is $V_m - V_g$. If V_m is greater than V_g it will require an expenditure of work to discharge the ion, the ion will not give up its charge, *i.e.*, there will be no continuous current through the gas unless the external potential difference is greater than $V_m - V_g$.

Now take the case of a negatively electrified ion giving up its charge to the anode; here an electron has to be taken from the ion and given up to the anode; to remove the electron requires an amount of energy equal to V_1, where V_1 is the work required to move an electron from the negatively charged ion, it will be less than the ionising potential. On the other hand, work equal to V_m is gained when the electron goes into the metal thus to effect the transference, work equal to $V_1 - V_m$ must be done, so there must be an external potential difference greater than $V_1 - V_m$ to keep up the current.

It would seem as if experiments on the potential required to effect the passage of electricity from the gas to the metal ought to give us the means of finding V_g and V_1, quantities which are of fundamental importance in the energetics of chemical combination. To illustrate the kind of effects we are considering, let us take the case of ionised mercury vapour, the ionising potential of mercury vapour is about 10 volts; I cannot find any direct measurements of the work required to extract an electron from liquid mercury, but inasmuch as mercury gives off electrons when exposed to light whose wave-length is not less than 2000, it can-

not be greater than about five volts; thus V_m is much less than V_g; thus a positively charged mercury atom could give up its charge to a liquid surface of mercury without the aid of an external potential difference. Unless, however, the work required to extract an electron from a negatively electrified mercury atom is less than half that required to extract it from a neutral one, V_1 would be greater than V_m and it would require an external electromotive force to make negatively electrified mercury atoms give up their charge to a mercury surface. Both the gas and the electrode can be varied in these experiments; thus if the gas were a strongly electronegative one, like chlorine, we should expect V_1 to be greater than V_m for a metal like sodium for which Richardson's value is 2.6 volts; if so, it would require an external electric force to make negative chlorine ions discharge to sodium and get free. The chlorine ion would cling to the sodium and combine with it, thus with chlorine ions and an electropositive metal as electrode, the anode would be more likely to be attacked by the chlorine than the cathode. To liberate the electron from the chlorine and get a neutral chlorine atom would require a potential difference at the anode equal to $V_1 - V_m$. At the cathode a positively electrified chlorine atom might not merely get neutralised by receiving one electron, but if V_1 were greater than V_m, work would be gained by the chlorine atom receiving a second electron from the metal. When an electron falls into an atom, light is emitted; the frequency of the light depending on the amount of loss of potential energy caused by the falling in of the atom, or what is the same thing, by the work required to eject the electron again. This work where a positively charged chlorine atom receives one electron and becomes neutral is measured by the ionising potential of the chlorine atom; when a neutral atom receives an additional electron it is measured by V_1. Thus, whenever, at the surface, say of an alkali metal, the transference of electrons from the metal to, say, chlorine atoms, is going on, light will be emitted; this light will fall upon the metal, and as these metals give large photoelectric effects, it may cause them to emit electrons. As the light is emitted quite close to the surface of the metal, it is quite likely that the intensity at the surface may be sufficient to produce measurable effects though the intensity of the light may be much too faint to be detected at distances large compared with the radius of an atom.

INTERMETALLIC COMPOUNDS.

The expression we have found for the potential energy of a solid has an important application to the theory of intermetallic compounds and alloys. Take the case of two metals, A and B, when they are apart they consist of lattices of atoms and electrons, and as we have seen may be regarded as built up of units, each unit containing a certain number of atoms, together with the appropriate number of electrons. Thus if the metal were monovalent there would be as many electrons as atoms; if it were divalent there would be twice as many, and so on. Suppose now that the metals were mixed under conditions which permitted free movement of the atoms and electrons. Then in the mixture in addition to the units consisting wholly of A or of B atoms, we may have units containing both A and B atoms. Thus to take a definite case, let A be sodium and B potassium, the unit might be a cube of side $2d$, built up of eight cubes; at the centres of these, atoms of sodium and potassium might be placed alternately, the electrons would be at the corners, the centres of the faces, and the centres of the edges, and at the centre of the large cube. Such a unit would certainly be formed at low temperatures if its potential energy were less than that due to four units of sodium and four of potassium when these metals were separated. Again we might have a cubical unit with the potassium atoms at the corners and the sodium atoms at the centres of the faces; in this unit there would be three sodium to one potassium atom. There are many other possible units with different proportions of sodium and potassium atoms. Whether such units will be formed or not is a question of the relation between the potential energy of such a unit and the potential energy of the atoms it contains when arranged so that the units contain only one kind of atom. The point I wish to emphasize is that the conditions which determine the formation of these metallic compounds are of quite a different kind from those which determine the formation of gaseous compounds containing one or more electronegative constituents. With these it is the valency conditions, such as may be expressed by the formation of octets, which govern the type of admissible compound; with the metals, on the other hand, the formation or not of a compound is determined by the potential energy possessed by a unit of the lattice system formed by the compound. As this potential energy depends on the number of electrons as well as

upon the number of atoms in the unit, and as the number of electrons depends upon the valencies of the atoms, valency will have an influence upon the type of compound, but of a different character to that exerted in compounds between metals and electronegative elements. From these considerations we should expect that the structure of intermetallic compounds would not conform to the condition of valency as ordinarily understood. We find, for example, many stable compounds in which two atoms of a bivalent metal are combined with one atom of a univalent one, *e.g.*, $NaCd_2$, KHg_2, $CuMg_2$, a proportion inconsistent with the usual conception of valency, but one which would be satisfied by a very simple form of unit cell. Thus if the divalent atoms were at the corners of a hexagonal prism and the monovalent atom at the centre, while the electrons were placed at the centres of side faces of the prism and two along the axis on either side of the monovalent atom, we have a unit containing two divalent atoms, one monovalent atom and five electrons.

MIXED CRYSTALS AND INTERMETALLIC COMPOUNDS.

Metallurgists distinguish between two types of combination between metals. The one type called intermetallic compounds consists of alloys of a composition at which on a graph representing the relation between percentage composition and some physical property, such as electrical conductivity, shows a well-marked maximum or minimum. These points in general correspond to alloys in which the proposition between the numbers of atoms of the two metals are expressed by simple ratios. Alloys of other composition represented by the regions between the maxima and minima are supposed to be in a state which is sometimes described as mixed crystals and sometimes as solid solutions.

Let us consider the question of the combination of two metals *A* and *B* from the point of view of the electron theory of solids. There are several possibilities, the alloy might be a mechanical mixture of *A* and *B;* by this we mean that the atoms of *A* and *B* are respectively arranged in their own space lattices, and that there are no composite space lattices made up of atoms of *A* and *B* arranged in regular sequence. Another alternative is that the atoms should be arranged in composite space lattices, the atoms along the lines of the lattices consisting partly of *A* atoms and partly of *B*. Here there are again several possibilities, for with a fixed proportion between the number of *A* atoms and

the number of B there are many different composite lattices possible. Thus, for example, if there are three A atoms for one of B, we might in two dimensional lattices have the spacings

I.

a a a a a a a a a
a b a b a b a b a
a a a a a a a a a
a b a b a b a b a

or

II.

a a a b a a a b a a a b a a a
a b a a a b a a a b a a a b a
a a a b a a a b a a a b a a a

or

III.

a a b a a b a a b a a b a a b
a a a a a b a a a a a b a a a
a a b a a b a a b a a b a a b

Thus the alloy might consist either of one kind of lattice or a mechanical mixture of a number of different kinds. If the atoms have been in a condition in which they could diffuse freely, *e.g.*, if the alloy were stirred for a long time when the melt was liquid, the arrangement would be that corresponding to minimum potential energy, remembering that when there is a mechanical mixture of different phases we must take into account the energy due to surface tension. When there is a well-marked minimum in the potential energy for one arrangement of the atoms, we should expect that the alloy would be homogeneous and represented by a single lattice corresponding to this arrangement. If, on the other hand, there are several arrangements which differ but little from each other in potential energy we might expect to find all these arrangements present in the alloy in proportions which would vary with the temperature. When the alloy is homogeneous and the arrangement of atoms and electrons capable of being represented by a single lattice, it corresponds in my view to an intermetallic compound. When, however, there are several different arrangements mixed together, it corresponds to a solid solution.

When the atoms of A and B carry the same charge of electricity, then if A is greatly in excess we should expect the B atoms to occupy positions along a space lattice that differed but little from that for pure A. When, however, the number of the

B atoms increase beyond a certain proportion, there will probably be large modifications in the space lattice for the mixture and possibly the formation of one of quite a different character. The probability of a new type of space lattice will be much increased if *B* and *A* carry different electrical charges, *i.e.*, have different valencies.

Let us consider from this point of view the changes we might expect in the properties of a mixture of two metals, *A*, *B*, starting from pure *A* and ending with pure *B*.

When *A* is greatly in excess, the formation of those compounds which contain a comparatively large proportion of *A* in comparison with *B* will, in accordance with the principles of mass action, be promoted, and the mixture will consist of free *A*, little or no free *B*, and a number of compounds, the majority of which contain an excess of *A* over *B*. As the proportion of *B* increases the amount of free *A* diminishes and the proportion between the amounts of different types of compounds changes, the change being mainly at the expense of those which contain a large number of *A* atoms. When the mixture is such that the proportion between *A* and *B* is that of a possible compound, if that compound is one which has markedly less potential energy than its constituents, the whole mass of metal at low temperatures at any rate may practically consist of this compound. It need not, however, do so in all cases; there may be a certain amount of dissociation of the compound depending upon the temperature. Again, if there is another compound with very small potential energy, some of it is pretty sure to be formed, so that the mixture may not be quite homogeneous even when the proportions are those of a possible compound. When the mixture consists almost entirely of one compound, its constitution is identical in many respects with that of a simple metal. All the units of which it is built up are of one kind, and that kind an arrangement of atoms and electrons, which when the units are united give, as in the cases of metals, a system of lattices for atoms and electrons. Any general property possessed by all metals would, we should expect, be possessed by this compound. In particular the conduction of electricity through the compound would take place by the same mechanism as through metals. Now one peculiarity of the conduction of electricity through metals is that the temperature coefficient of the electrical resistance is much the same for all

metals, hence we should expect that the temperature coefficient of an intermetallic compound would be about that of the pure metals. There seems to be very considerable evidence [36] that this is approximately true.

The temperature coefficient of the electrical resistance when the mixture of the two metals contains several compounds is often very much smaller than that for pure metals; in fact, it is even sometimes of opposite sign. When there are several different components the effect of a rise in temperature will be an increase in the dissociation and hence an alteration in the proportion of the amount of different compounds present in the alloy. The more complicated compounds will be split up by the rise in temperature and the proportion of simpler ones increased. As the lattices formed by the complex compounds are more intricate than those of the simpler ones, we should expect their electrical resistance to be greater so that when some of these are split up owing to the rise in temperature there will be a tendency to reduce the resistance. Thus in a mixture of this kind there is, in addition to the normal effect which makes the resistance increase, an effect tending to make the resistance fall when the temperature rises; this will diminish the temperature coefficient of the resistance.

Let us now consider the changes in the elastic properties produced by the formation of these intermetallic compounds. We have seen that in the solid state the potential energy of an atom and its associated electrons is equal to

$$-4.5\,\frac{k_A}{N_A} \tag{92}$$

when k_A is the bulk modulus and N_A the number of atoms in unit volume for the element A, since $N_A = \triangle_A / M_A$ where $\triangle_A$ is the density of A and M_A the mass of its atom, the potential energy per atom may be written as

$$-4.5\,k_A\,\frac{M_A}{\triangle_A} \tag{93}$$

Thus the potential energy of n atoms of a metal A and m of a metal B before they combine is equal to

$$-4.5\left(k_A\,\frac{nM_A}{\triangle_A} + k_B\,\frac{mM_B}{\triangle_B}\right) \tag{94}$$

[36] "Desch. Intermetallic Compounds," p. 52.

If these unite to form the compound A_nB_m, the potential energy per molecule of this compound is

$$-4{\cdot}5\,\frac{k_{nm}}{\Delta_{nm}}\,(nM_A+mM_B) \tag{95}$$

Where k_{nm} is the bulk modulus of the compound and Δ_{nm} its density, thus by the formation of the compound, the diminution of potential energy per molecule of the compound formed is

$$4{\cdot}5\left\{\frac{k_{mn}}{\Delta_{mn}}(nM_A+nM_B)-\left(\frac{nk_AM_A}{\Delta_A}+\frac{mk_BM_B}{\Delta_B}\right)\right\} \tag{96}$$

and this must be equal to the heat of formation per molecule of the compound at zero absolute temperature. Thus from the compressibilities of the compound and those of its constituents we can calculate the heat of formation of the compound.

Again

$$\frac{nk_AM_A}{\Delta_A}+m\,\frac{k_BM_B}{\Delta_B}=K\left(\frac{nM_A}{\Delta_A}+\frac{mM_B}{\Delta_B}\right) \tag{97}$$

and

$$\frac{nM_A}{\Delta_A}+\frac{mM_B}{\Delta_B}=\frac{nM_A+mM_B}{\Delta} \tag{98}$$

Where K is the bulk modulus and Δ the density of the mixture, calculated on the assumption that A and B exert no influence on each other, hence the diminution in potential energy due to the formation of the compound may be written in the form

$$4{\cdot}5\,(nM_A+mM_B)\left\{\frac{k_{mn}}{\Delta_{mn}}-\frac{K}{\Delta}\right\} \tag{99}$$

Now the compound will not be formed unless the potential energy diminishes, hence $\frac{k_{mn}}{\Delta_{mn}}-\frac{K}{\Delta}$ must be positive, or if, as is generally the case, Δ_{mn} is very nearly equal to Δ, k_{mn} must be greater than K; in other words, the compound must be less compressible than a mechanical mixture of the metals. It is a general rule that the "hardness" of an alloy is greater than we should expect from its composition, and though hardness is not the same thing as the reciprocal of the compressibility yet some of the tests used to measure the hardness, *e.g.*, the indentation produced by a loaded ball, seem almost more a test of compressibility, the result that combination diminishes the compressibility seems to be indicated.

RADIATION AND CHEMICAL REACTION.*

BY

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THE problem of the emission and absorption of radiation by matter is foremost in the minds of the physicists and chemists of the present day. An exact knowledge of these phenomena implies an exact knowledge of atomic and molecular constitution as well as an exact knowledge of the nature and properties of radiation. Even with such achievements as the Planck radiation formula, the Bohr-Sommerfeld theory of emission spectra, the Debye theory of the atomic and molecular heats of solids in the background, it may be said that only the first steps have been made toward a solution of the problem.

Very closely associated with this development is the obscure and complicated field of chemical reactivity. Every further approximation to exactness in the studies of atomic structure and the nature of radiation premises an advance in a knowledge of the mechanism of chemical reactions, and, *vice versa,* any advances made in the study of chemical reactivity will supplement the knowledge of matter and radiation. In this field, at least, the intellectual interests of the physicists and chemists are identical.

In order to make progress in such a field, it is of great value to have a working hypothesis, founded on the best laws and evidence available, and containing in it ideas, which, whether true or false, possess such a dynamic character as to suggest numerous experiments. The "radiation theory" of chemical reactivity suggested and developed by Trautz, W. C. McC. Lewis, and Perrin, and later further criticized and ramified by Tolman and Dushman, possesses these characteristics. In the following, a brief presentation of this theory and some of its implications will be made.

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(1) THE REACTION VELOCITY CONSTANT OF HOMOGENEOUS REACTIONS.

According to the law of Guldberg and Waage, the velocity of a chemical reaction may be expressed by the equation

$$\frac{dm}{dt} = k_1(m_1 m_2 m_3 \cdots m_n) \qquad (1)$$

where $\frac{dm}{dt}$ is the velocity at a time t and m_1, m_2, m_3, . . . m_n are the masses of the atomic, molecular, or ionic species present at a time t. When only one species is changing, the reaction is monomolecular, when two species are changing, the reaction is bimolecular and so forth. k_1 is the reaction velocity constant. From the point of view of the student of reaction velocities, it may be said that no two chemical reactions may be expected to have the same velocity constants, and no laws are known which enable the prediction of the numerical value of the velocity constant of an unknown reaction.

Reactions may be divided into two types:

(1) Reactions which have a very high temperature coefficient of reaction velocity constant, or *thermal reactions*, and (2) reactions which have a very low or inappreciable temperature coefficient of reaction velocity, or *photochemical reactions*. An example of a monomolecular reaction of the first type is the thermal decomposition of phosphine in the gaseous phase. An example of a reaction of the second type is a photochemical reaction such as

$$H_2 + Cl_2 = 2HCl$$

where visible radiation causes combination and ultra-violet radiation causes decomposition. Incidentally, the rate of decomposition of radioactive elements is a monomolecular reaction obeying the well-known law

$$k_1 = \frac{1}{t}\ln\frac{I_0}{I} \text{ or } I_0 e^{-k_1 t} = I \qquad (2)$$

where k_1 is the velocity constant, e is the base of the natural logarithm, I is the radioactive intensity at a time t, and I_0 is the initial intensity. (The intensity is proportional to m, the mass of radioactive substance.) The rate of radioactive decomposition is independent of the temperature, and, consequently, according to the above classification, radioactive changes should be *photochemical*.

Any combination of two molecules to form one or more species is a bimolecular reaction. Thus, the thermal combination of hydrogen and iodine in the vapor phase to form gaseous hydriodic acid is an example. Other familiar examples are the hydrolysis or the saponification of an ester, the hydrolysis of cane sugar, etc.

(2) THE TEMPERATURE COEFFICIENT OF THE REACTION VELOCITY CONSTANT OF MONOMOLECULAR THERMAL REACTIONS.[1]

The velocity constant of a thermal reaction doubles or trebles with a rise of temperature of 10° C. This extraordinary rise in velocity has proved very difficult to explain. Take, for example, any monomolecular reaction, in which one molecular species and only one is changing (the decomposition of phosphine), and consider how a change is brought about. If only the molecules in the reacting chamber and nothing else be taken into account, there are two alternatives: (1) That the molecules decompose spontaneously without being influenced by an external agency; (2) that a molecule decomposes after collisions with other molecules, by means of some kind of molecular shock. Spontaneous decomposition is untenable, because such an assumption involves difficulties in the energy relations, and it would be extremely difficult to explain the increasing explosibility of the molecule with rise in temperature. The theory that the molecule decomposes at each collision with another molecule is also untenable, for, in the first place, it can be shown by kinetic calculations of the change in number of such collisions with the temperature that a rise in 10° C. would only increase the velocity constant about 3 per cent. Substantiating this is the extremely important fact that, at a given temperature, the velocity constant of a monomolecular reaction is indepèndent of the pressure. Further, if molecular shock produced an increase in velocity, the presence of many molecules of an inert substance (argon in the phosphine) would increase the velocity. This, in cases of monomolecular gas reactions, has been shown not to be the case.

In attempting to explain these phenomena, mention should first be made to a simple and brilliant suggestion made by Arrhenius. This was that an ensemble of molecules of any substance at a given temperature contains inactive and chemically

[1] Perrin, *Annales de Physique*, Ser. 9, 11, 5 (1919).

active molecules, and that increase in temperature increases the number of active molecules. It was also shown by Arrhenius that the expression

$$\frac{d \ln k_1}{dT} = \frac{A}{T^2} \qquad (3)$$

accounts for the variation of the reaction velocity constant with the temperature in a satisfactory manner. In this equation, k_1 is the velocity constant, A is a constant, and T is the absolute temperature.

In all the previous discussion concerning the monomolecular gas reaction, one very important consideration has been omitted. If a gas is in a hollow space at a given temperature, there is present in this "hohlraum," not only the gaseous molecules but thermal radiation of various wave-lengths and of density corresponding to that temperature. As will be shown in the following section, in considering the kinetics of chemical reactions, not only the mechanism of the reaction but also the mechanism of the radiation, and the exchange of energy between the matter and the bath of radiation must be taken into account.

(3) THE RADIATION HYPOTHESIS OF CHEMICAL REACTIONS.

The idea that radiation is the source of the energy which activates all chemical reactions was first proposed by Trautz.[2] This point of view has been more clearly stated and generalized by Lewis[3] and by Perrin.[4]

Following Perrin, the radiation hypothesis may be stated as follows: "All chemical reaction is provoked by a radiation; its velocity is determined by the intensity of that radiation, and only depends on the temperature in the measure that the intensity depends on it." This statement involves a number of questions of interest. Radiation is here meant in the broadest sense, including all modes of vibration, extending from the extremely short wave-lengths into the longest wave-lengths in the infra-red. In general, visible and ultra-violet absorption or emission is to be associated with the electrons, infra-red absorption or emission

[2] *Zeits. Photo.*, **4**, 160 (1906); *Zeits. anorg. Chemie*, many articles from 1906 to the present time. See bibliography at the end of this article.

[3] *Jour. Chem. Soc.*, numerous articles from 1914 to the present time.

[4] "Les Atomes," 1913, *Annales de Physique*, (9), **11**, 5 (1919).

with the atoms and molecules. Consequently, purely thermal reactions will be activated by the infra-red. In the second place, the reaction velocity is assumed to be proportional to the intensity of radiation, or the radiation density.[5] This is the simplest assumption.

According to the above hypothesis, the rate of a monomolecular reaction will be given by

$$\frac{dx}{dt} = \text{constant } (a - x)\, u_\nu d\nu \tag{4}$$

where x is the mass of substance changed in a time t, a is the initial mass of substance, and $u_\nu d\nu$ is the radiation density. Planck's radiation formula is

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1}\, d\nu = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}\, d\nu \tag{5}$$

where $u_\nu d\nu$, the radiation density, is the energy density of all modes of vibration with frequencies between ν and $\nu + d\nu$. h is the Planck constant, c is the velocity of light, e is the base of the natural logarithm, k is the gas constant per molecule, and T is the absolute temperature. By means of Fourier series and probability considerations, it can be shown that the number of modes of vibration in unit volume of frequencies between ν and $\nu + d\nu$ is $\frac{8\pi\nu^2}{c^3} d\nu$. According to the quantum theory, the energy of a mode of vibration of a frequency ν is $\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$. The product of these two quantities gives the energy of unit volume of radiation of frequency ν. Since π, h, ν, and c are constant, and $d\nu$ is taken for a small finite band of frequencies, the reaction velocity may be written

$$\frac{dx}{dt} = \text{constant } (a - x) \frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{6}$$

[5] It is worthy of note that Einstein (*Ann. der Physik*, (4), **37**, 832 (1912)), in the deduction of the photochemical equivalent law makes the same assumption that the photochemical reaction rate is proportional to the density of visible or ultra-violet radiation. The radiation hypothesis may, therefore, be regarded as an extension of the Einstein photochemical equivalent law to thermal reactions.

Perrin and Lewis take it that in the infra-red region $\frac{1}{e^{\frac{h\nu}{kT}} - 1}$ may be put equal to $e^{-\frac{h\nu}{kT}}$ without making an appreciable error. The radiation density would also be proportional to $e^{-\frac{h\nu}{kT}}$ if Wien's radiation formula had been employed. Then

$$\frac{dx}{dt} = \text{constant}\,(a - x)\,e^{-\frac{h\nu}{kT}} \tag{7}$$

Integrating at constant temperature

$$\frac{1}{t}\ln\frac{a}{a - x} = \text{constant}\,e^{-\frac{h\nu}{kT}} = k_1 \tag{8}$$

where k_1 is the observed velocity constant. Differentiation of this last equation with respect to T gives

$$\frac{d\ln k_1}{dT} = \frac{h\nu}{kT^2} \tag{9}$$

Remembering that $k = \frac{R}{N}$, where R is the gas constant per gram molecule, and N is Avogadro's number, we obtain finally

$$\frac{d\ln k_1}{dT} = \frac{N h\nu}{RT^2} \tag{10}$$

This important equation has here been derived in a simple manner from the radiation hypothesis with the further assumption of the quantum theory. ν is the frequency which provokes the reaction and is assumed by Perrin and Lewis to be a single frequency or a narrow band of frequencies. To sum up, it is found that by making the velocity constant proportional to the energy density of thermal radiation, an equation similar in form to the equation of Arrhenius may be deduced.

The same reasoning may be applied to polymolecular reactions. Take the reaction

$$A_1 \longleftarrow A'_1 + A'_2$$

The reaction velocity of combination at constant temperature will be given by

$$v = k' C_{A'_1} C_{A'_2}$$

The temperature coefficient of bimolecular reactions is of the

same order of magnitude as of monomolecular reactions. This large temperature coefficient is not accounted for by the theory of molecular collisions, and, consequently, it is reasonable to assume that the bath of radiation plays a similar rôle in the mechanism of bimolecular and monomolecular reactions.

It is important to know whether ν calculated by this equation and observed velocity constants always falls in the infra-red region. This point is confirmed by the following table taken from Perrin's paper:

TABLE I.

Frequencies and Wave-lengths Calculated by Equation (10).

Reaction.	Temperature Range.	$\nu \times 10^{-14}$	Ångstrom Units.
Saponification of ethyl acetate...	9 ⟶ 45	1.17	25,600
Dissociation of PH_3	310 ⟶ 510	1.2	25,000
$KClO_3 + FeSO_4 + H_2SO_4$	10 ⟶ 32	1.61	18,600
$C_2H_5ONa + CH_3I$	6 ⟶ 30	1.97	15,200
$HPO_3 + H_2O$	0 ⟶ 61	2.0	15,000
$CH_3CONH_2 + H_2O$	65 ⟶ 100	2.0	15,000
$CH_2ClCH_2OH + KOH$	24 ⟶ 44	2.14	14,000
Dibromsuccinic acid + H_2O	15 ⟶ 101	2.34	12,800
Diazoaminobenzene ⟶ azoaminobenzene	25 ⟶ 35	2.4	12,500
$COS + H_2O$	15 ⟶ 40	2.4	12,500
Inversion of cane sugar	25 ⟶ 55	2.68	11,200
$CH_2ClCOONa + NaOH$	70 ⟶ 130	2.75	10,900
$CH_2ClCOOH + H_2O$	80 ⟶ 150	2.77	10,800
Dissociation of AsH_3	256 ⟶ 364	2.80	10,000

All wave-lengths correspond to the infra-red region.

(4) INFERENCES FROM STATISTICAL MECHANICS.

It has been shown by Marcelin[6] and Rice[7] from considerations of statistical mechanics, that the velocity constant of a thermal reaction will be expressed as a function of the temperature by the equation

$$\frac{d \ln k_1}{dT} = \frac{E_c}{RT^2} \qquad (11)$$

[6] *Comp. Rend.*, **157**, 1419 (1913); **158**, 116 and 407 (1914); *Ann. de Physique*, (9), **3**, 120 (1915).

[7] *Brit. Asso. Rep.*, 1915, 397.

This equation is of the same form as the equation of Arrhenius and equation (10), but, in this case, a further significance is given to the quantity E_c. Rice showed that E_c equalled the difference between the energy of 1 mol of activated molecules and the average energy of 1 mol of molecules. Tolman [8] has shown, by a somewhat different mathematical treatment, that

$$\frac{d \ln k_1}{dT} = \frac{\overline{E}_A - E_A + \overline{E}_R - E_R}{RT^2} \qquad (12)$$

where $\overline{E}_A$ is the average energy of the molecules which enter reaction, E_A is the average energy of all molecules of this kind, $\overline{E}_R$ is the average energy of the modes of vibration upon entering the reaction, and E_R is the average radiant energy of such modes of vibration whether or not they are in a reactive condition. This equation becomes

$$\frac{d \ln k_1}{dT} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2} = \frac{E_c}{RT^2} \qquad (13)$$

where E_c, the critical increment, is the energy causing the decomposition of 1 mol of molecules through interaction with "1 mol" of modes of vibration, and E_{average} is the average energy of the molecules and modes of vibration. This latter equation, as well as that of Marcelin and Rice, is of considerable interest because it has been deduced without the assumption of the quantum theory, and the integration has been carried out, not for a narrow range of frequencies, but for all frequencies, and all states of the molecules and modes of vibration. Further, since this equation is similar in form both to the equation of Arrhenius, and to the equation derived by Lewis and Perrin from the radiation hypothesis, it is of considerable value to state, without going into particulars, the assumptions upon which it is based and the method of derivation.

The Maxwell distribution law, which gives the number of elements (molecules or modes of vibration) out of a total number of elements which have coördinates and momenta in an element of volume of generalized space, was deduced by the usual method. The Hamiltonian equations of motion were assumed. The probability of a state described statistically was found, and this probability made a maximum, corresponding to statistical equi-

[8] *Jour. Amer. Chem. Soc.*, **42**, 2506 (1920).

librium. This involved the use of Stirling's formula for factorials. In applying the Maxwell distribution law to the rate of monomolecular thermal reactions and their temperature coefficients, the following assumptions were made:

(1) The system is gaseous.

(2) The velocity slow and measurable.

(3) Dilute.

(4) Radiation is a necessary part of the reaction. The chance that a molecule will absorb radiation depends on the states of the molecule and the bath of radiation. Thus, the present deduction depends on the radiation theory, but not on the quantum theory.

(5) The integration is to be carried out over all frequencies and all possible states of molecules and modes of vibration. Not a single frequency, or a narrow band of frequency, but all frequencies may cause activation.

For the temperature coefficient of a truly photochemical reaction activated by a narrow range of frequencies, Tolman obtains the equation

$$\frac{d \ln k_1}{dT} = \frac{\overline{E}_A - E_A}{RT^2} \tag{14}$$

where $\overline{E}_A$ is the energy of the molecules which react and E_A the average energy of the molecules. This temperature coefficient will be very small or perhaps inappreciable.

(5) THE VAN'T HOFF EQUATION.

A chemical reaction represented by

$$A_1 + A_2 + \cdots \rightleftarrows A'_1 + A'_2 + \cdots$$

will be in dynamic equilibrium when the velocity from right to left equals the velocity from left to right, and, consequently,

$$v_1 = v'_1 = k_1 c_{A_1} c_{A_2} \cdots = k_2 c_{A'_1} c_{A'_2} \cdots$$

where v_1, v'_1, are the velocities from left to right and from right to left, respectively; k_1 and k_2 the velocity constants from left to right and from right to left, respectively, and the c's represent the concentrations of the molecular species denoted by subscripts. From this equation, it follows that

$$\frac{k_1}{k_2} = \frac{c_{A'_1} c_{A'_2} \cdots}{c_{A_1} c_{A_2} \cdots} = K \tag{15}$$

where K is the equilibrium constant of the reaction.

From statistical mechanical considerations, it has been found that

$$\frac{d \ln k_1}{dT} = \frac{E_1 \text{ activated} - E_1 \text{ average}}{RT^2} = \frac{E_{c_1}}{RT^2}$$

and

$$\frac{d \ln k_2}{dT} = \frac{E_2 \text{ activated} - E_2 \text{ average}}{RT^2} = \frac{E_{c_2}}{RT^2}$$

Since, at equilibrium, $E_{1\text{activated}}$ equals $E_{2\text{activated}}$,

$$\frac{d \ln \frac{k_1}{k_2}}{dT} = \frac{d \ln K}{dT} = \frac{E_2 \text{ average} - E_1 \text{ average}}{RT^2} = \frac{\triangle E}{RT^2} \tag{16}$$

It is readily seen that $\triangle E$ is the increase in internal energy of the reaction in going from left to right. Equation (16) was first obtained by Van't Hoff by purely thermodynamic reasoning applied to a reaction taking place in a homogeneous system of gases.

(6) SUMMARY AND CONSEQUENCES OF THE PRECEDING DISCUSSION.

From the preceding equations, all the important fundamental equations resulting from the radiation hypothesis may easily be derived.

(1) By the assumption that the velocity of a thermal reaction was proportional to the radiation density, calculated by Planck's formula, the equation

$$\frac{d \ln k_1}{dT} = \frac{Nh\nu}{RT^2} \tag{10}$$

has been deduced.

(2) By applying statistical mechanics to the problem of thermal reaction rate,

$$\frac{d \ln k_1}{dT} = \frac{E_c}{RT^2} \tag{11}$$

may be deduced, where E_c is the energy necessary to activate a gram molecule.

From these equations, it follows that if the reaction is stimulated by a single frequency or a narrow range of frequencies,

$$E_c = Nh\nu \tag{17}$$

remembering that, by equating these quantities, the quantum theory is tacitly assumed. Equation (17) is an expression of the Einstein photochemical equivalent law for thermal reactions, and states that to produce the decomposition of a single molecule, one quantum of energy, $h\nu$, corresponding to a frequency ν, must be absorbed.

(3) From Van't Hoff's equation and equation (10), the following is obtained

$$\frac{d \ln \frac{k_1}{k_2}}{dT} = \frac{Nh\nu_1 - Nh\nu_2}{RT^2} = \frac{\triangle E}{RT^2} \tag{16}$$

whence

$$\triangle E = Nh(\nu_1 - \nu_2) \tag{18}$$

This formula for the internal energy change of a reaction was originally deduced by Haber [9] by a different method. If equation (18) be applied to chemical reactions, then, following the nomenclature of Perrin, all monomolecular chemical reactions should be written in the form

$$Nh\nu_1 + A = A' + Nh\nu_2 \tag{19}$$

where ν_1 is the frequency which activates A causing its decomposition, and ν_2 is the frequency which activates A' and causes its decomposition. Tolman, as previously mentioned, has investigated the case of thermal reactivity where all frequencies may cause activation.

It must be borne in mind that $\triangle E$ varies with the temperature. This fact is not explained by equations (18) and (19).

(7) SOME THEORETICAL CONSEQUENCES OF EQUATION (19). PERRIN'S EXTENSION OF THE RADIATION HYPOTHESIS.

Following the procedure of Perrin, all monomolecular reactions should be written according to

$$Nh\nu_1 + A = A' + Nh\nu_2 \tag{19}$$

A polymolecular reaction would also be written in the same general way, being probably more complicated than the above by reason of the absorption and emission of more frequencies by more molecular species. This equation is regarded as being valid not only for thermal reactions, but for all reactions where the absorb-

[9] *Ber. Deutsch. phys. Gesel.*, 13, 1117 (1911).

ing or emitting oscillator may be either the atom or the electron. The mechanism of all reactions is therefore fundamentally a universal photochemical mechanism. "All chemical reaction consists of two movements: The absorption of radiant energy which provokes the reaction and the emission of radiation by the reverse reaction." In his admirable defense of this thesis, Perrin has applied the theory to such diverse phenomena as phosphorescence, fluorescence, radioactivity, the evolution of the stars, velocity of crystallization, fusion pressures, sublimation, evaporation, emission and absorption spectra, etc. A few of these examples will suffice to illustrate his method.

(*a*) *The Quantum Theory.*—When an ensemble of molecules and atoms undergoes a change, the rate of this change can be measured, due to the fact that all the molecules and atoms are not capable of reacting at once. When, however, the change in a single molecule or atom, or the change within a single molecule or atom is considered, the rate of change is extremely great, and immeasurable. From the following postulates, which give a picture of this mechanism, the quantum theory may be deduced:

(1) Matter consists of electrons and positive nuclei, and these elementary oscillators cause the emission and absorption of radiant energy.

(2) These charges are grouped in stable states which do not radiate, and, when in this condition, are atoms and molecules.

(3) Atoms are capable of passing from one stable state to another stable state with great rapidity, thus emitting or absorbing radiation.

(4) The variation of energy is $h\nu$ where ν is the absorbed or emitted frequency and h is Planck's constant.

Thus, a reaction consists of an ensemble of extremely rapid changes from one stable state to another. When a molecule or an atom passes from a stable state a to a stable state a', $h\nu$ energy is first absorbed by the system in the state a rendering it unstable or active. This absorption will depend on the frequency of oscillation of the atoms or electrons of the system, and the phase, the intensity of the radiation, and, perhaps, some other factors. The unstable state a then changes to the state a' with extreme rapidtiy, liberating $h\nu'$. The total energy change is $h\nu - h\nu'$. According to Perrin's point of view, there are no exceptions to this picture.

(*b*) *The Bohr Theory of Emission Spectra.*—If it is assumed, as Bohr assumes, that the atom may exist in a successive series of stable states

$$a_1, a_2, a_3 \cdots a_n$$

possessing internal energies

$$U_1, U_2, U_3 \cdots U_n$$

and that

$$U_n \cdots > U_3 > U_2 > U_1$$

the radiation theory of Perrin falls into accord with the Bohr theory. For let each of the stable states correspond to definite electronic arrangements, electronic orbits. Then, if an electron passes from a_5 to a_3, the energy emitted is according to the Bohr theory

$$U_5 - U_3 = h\nu'$$

It is hard to understand this spontaneous change or jump from one stable state to another without the agency of an external stimulus. The application of the fundamental equation

$$\overrightarrow{h\nu} + A \longrightarrow A' + \overrightarrow{h\nu'}$$

removes this difficulty. Thus, light of a frequency $\frac{U_5 - U_2}{h}$ may transform an atom from a state a_2 to a state a_5. If the electron then falls into an inner orbit, or a state a_3, the frequency $\frac{U_5 - U_3}{h}$ would be emitted. This whole process may be written

$$\overrightarrow{h\left(\frac{U_5 - U_2}{h}\right)} + a_2 \longrightarrow a_3 + \overrightarrow{h\left(\frac{U_5 - U_3}{h}\right)}$$

(*c*) *Radioactive Transformations.*—Since equation (19) is held to be valid for all transformations of matter, it should be valid for radioactive decompositions. Radioactive changes apparently take place spontaneously according to the law of monomolecular change. The rate is independent of the temperature and all other external conditions. At first glance these changes are like explosions, taking place with an enormous evolution of heat. Radioactive change has thus always been supposed to be exothermic.

Perrin assumes that the decomposition of radioactive atoms is not exothermic but endothermic, and is produced by the absorption

of radiations of very high frequencies ($v = 10^{21}$ or 1000 times the frequencies of X-rays). These rays traverse all substances, and are formed in the incandescent centre of the earth. Radiation of such frequency will not exist in ordinary thermal radiation, and thus radioactive decomposition will be independent of the temperature. The process may be expressed by

$$\overrightarrow{Nhv} + Ra \longrightarrow RaEm + He + Nhv'$$

where v is radiation of this enormous frequency, and v' is the frequency of the thermal radiation emitted. From the above equation

$$Ra \longrightarrow RaEm + He - Nh(v - v')$$

and, consequently, the reaction takes place with the absorption of energy equal to $Nh(v - v')$. In this ingenious way, the theory may be applied to radioactive phenomena, and the difficulty of explaining spontaneous explosibility avoided.

(8) THE EINSTEIN PHOTOCHEMICAL EQUIVALENT LAW.

The Einstein photochemical equivalent law may be stated as follows: If a gram molecule of any substance is decomposed by luminous or ultra-violet radiation of frequency v, Nhv radiation energy must be absorbed by the substance. This law was originally deduced by Einstein for purely photochemical reactions by a method quite different from the method employed in the present discussion. In Einstein's deduction, however, the same fundamental assumption as that underlying the radiation hypothesis, namely, that the reaction rate of a photochemical reaction is proportional to the density of the radiation absorbed. This assumption, which is the simplest, is made in all these theories.

Many investigations of photochemical reactions reveal that for certain reactions which Bodenstein [10] has conveniently called primary reactions, the photochemical equivalent law holds within the limit of experimental error. In Table II are given a few examples selected from the collection of data presented by Bodenstein and Dux.

[10] Bodenstein and Dux, *Zeits. Physik. Chem.*, **85**, 297 (1913).

TABLE II.

Primary Photochemical Reactions.

Reaction.	Absorption.	Law of Velocity.	$\frac{h\nu}{\text{Molecule}}$
$3O_2 = 2O_3$	Weak	k_1 (O_2)	4
	Strong	k_1	
$2NH_3 = N_2 + 3H_2$	Strong	k_1	1 for 2 NH_3
Anthracene $\longrightarrow$ dianthracene	Medium	$k_1 I$	0.7 $\longrightarrow$ 1.0
$S\lambda = S_u$	Medium	$k_1 I$	4 $\longrightarrow$ 5 (approx.)

(I is the light intensity; (O_2) is the concentration of oxygen molecules.)

These results are of the right order of magnitude, and, since any direct method of measuring the energy absorbed is difficult, may be considered as good evidence for the law. In these reactions, the equivalence of the exchange of energy between the radiation and matter appears to be established.

There are, however, a class of reactions, secondary light reactions, which are exceptions to the photochemical equivalent law. A few examples, selected from Bodenstein's and Dux's paper, are given in Table III.

TABLE III.

Secondary Photochemical Reactions.

Reaction.	Law of Velocity.	$\frac{\text{Molecules}}{h\nu}$
$H_2 + Cl_2 = 2HCl$	$\frac{k_1 (Cl_2)^2}{(O_2)}$	10^6
$2O_3 = 3O_2$	$\frac{k_1 (O_3)^2}{(O_2)}$	$10^2 \rightarrow 10^3$
$4HI + O_2 = 2H_2O + 2I_2$	$k_1 [I_2] [O_2]$	10^6
$Br_2 + C_7H_8 = C_7H_7Br + HBr$	$k_1 [Br_2] [C_7H_8]$	10^6

In three of the above reactions, for 1 $h\nu$ absorbed, 10^6 molecules react.

Notable attempts have been made by Bodenstein and Nernst to explain this enormous discrepency. Bodenstein's theory was based on an assumed photoelectric effect on the molecules. Nernst [11] admits that all primary photochemical reactions conform to the Einstein photochemical equivalent law. In the case

[11] *Zeits. Elektrochemie*, 24, 335 (1918).

of secondary light reactions, secondary reactions of an obscure nature take place. Nernst explains the photochemistry of the reaction of formation of hydrogen chloride from hydrogen and chlorine as follows:

(1) The primary reaction which obeys the Einstein law is

$$Cl_2 = 2\,Cl$$

(2) Two secondary reactions take place simultaneously, which are

$$Cl + H_2 = HCl + H$$
$$Cl_2 + H = HCl + Cl$$

According to the above processes, from an extremely small number of chlorine atoms, a relatively large number of hydrogen chloride molecules may be formed. This explains also why this reaction is retarded by the presence of traces of impurities such as ammonia.

The primary light reaction liberates atoms. If there is present in the system "acceptors" or molecules easily capable of reaction with these atoms, very many molecules may be formed per quantum of light absorbed. If there is no acceptor present, fewer molecules may react than required by the photochemical equivalent law. This point is in accord with the experiments of Pusch [12] on the reactions between hydrogen and bromine and hexahydrobenzene and bromine.

All the above examples refer to true photochemical reactions brought about by the absorption of visible or ultra-violet light. No direct evidence of the kind has been contributed for the establishment of the law for reactions stimulated by infra-red radiation. The behavior of thermal reactions may be proved to be quite different.

(9) DUSHMAN'S THEORY.[11]

From statistical mechanical and thermodynamic theory, it has been found that

$$\frac{d \ln K}{dT} = \frac{\triangle E}{RT^2} = \frac{E_1 - E_2}{RT^2} \tag{16}$$

and

$$\left.\begin{aligned} \frac{d \ln k_1}{dT} &= \frac{E_1}{RT^2} \\ \frac{d \ln k_2}{dT} &= \frac{E_2}{RT^2} \end{aligned}\right\} \tag{11}$$

[11] *Zeits. Elektrochemie*, **24**, 336 (1918).
[12] *Jour. Amer. Chem. Soc.*, **43**, 397 (1921).

K is the equilibrium constant of the reaction, $\triangle E$ the heat of reaction, k_1 is the velocity constant in one direction, k_2 the velocity constant in the reverse direction, and E_1 and E_2 are the heats of activation per mol. Before a reaction can occur in one direction or the other, the molecules must have acquired an energy E_1 or E_2 in excess of the average energies of the molecules. The fraction of the total molecules, N, which have acquired this energy may be calculated by means of the Maxwell distribution law for energies. Thus, the number of molecules dN_E which possess an energy between E and $E + dE$ is given by the equation

$$dN_E = \frac{N}{E_0} e^{-\frac{NE}{RT}} dE \tag{20}$$

If N is Avogadro's number, R will be the gas constant per mol. Let the mean initial energy of 1 mol of the molecules be E_{average} and let this energy be increased to the critical value E by the amount E_1 by the absorption of "1 mol" of radiation. The fraction α_E of the molecules which have a critical energy E will be given by

$$\alpha_E = \frac{\int_E^\infty \frac{N}{E_0} e^{-\frac{E}{RT}} dE}{\int_0^\infty \frac{N}{E_0} e^{-\frac{E}{RT}} dE} = \frac{-RTe^{-\frac{E}{RT}}\Big]_E^\infty}{-RTe^{-\frac{E}{RT}}\Big]_0^\infty} = e^{-\frac{E}{RT}}$$

Likewise, the fraction, $\alpha_{E\ \text{average}}$, of the N molecules which have an energy E_{average}, will be

$$\alpha_{E\ \text{average}} = e^{-\frac{E\ \text{average}}{RT}}$$

Then the fraction, $\alpha_E - \alpha_{E\ \text{average}}$, which have received the energy E_1 will be

$$\alpha = e^{-\frac{E}{RT}} - e^{-\frac{E\ \text{average}}{RT}} = e^{-\frac{(E - E\ \text{average})}{RT}} = e^{-\frac{E_1}{RT}} \tag{21}$$

If the reaction velocity constant, k_1, is assumed to be proportional to α, the equation

$$k_1 = \nu e^{-\frac{E_1}{RT}} \tag{22}$$

is obtained. k_1 has the dimension of t^{-1} or a frequency. The quantity E_1 has been shown to equal $Nh\nu_1$, the energy acquired

by the absorption of a frequency v_1. Therefore

$$k_1 = ve^{-\frac{Nh\nu_1}{RT}} = ve^{-\frac{h\nu_1}{kT}} \tag{23}$$

where $k = \frac{R}{N}$, an equation similar to equation (10).

Dushman's theory rests on the following assumptions:

(1) v in equation (23) is a frequency.

(2) The relation $E_1 = Nh\nu_1$ is valid.

(3) Dushman finally makes the bold assumption that

$$v = \nu_1 = \frac{E_1}{Nh} \tag{24}$$

As a result of the above considerations and assumptions, the velocity of a monomolecular reaction will be given by

$$-\frac{dc}{dt} = cv_1e^{-\frac{h\nu}{kT}} \tag{25}$$

and the velocity constant by

$$k_1 = v_1e^{-\frac{h\nu}{kT}} = \frac{E_1}{Nh}e^{-\frac{E_1}{RT}} \tag{26}$$

If the reaction be carried out at constant volume, E_1 will equal Q_1, the heat of activation, and thus Dushman's equation for the velocity constant of a monomolecular reaction is

$$k_1 = \frac{Q_1}{Nh}e^{-\frac{Q_1}{RT}} \tag{27}$$

Dushman has been able to show that this equation accounts for the present available data with considerable accuracy. Herein lies the justification of his assumptions. In the following, a calculation of the velocity constant of the dissociation of phosphine, taken from Dushman's paper, is given.

$$N = 6.062 \times 10^{23}$$

$$h = \frac{6.55 \times 10^{-27}}{4.184 \times 10^{7}}$$

Hence from equations (25) and (27)

$$k_1 = -\frac{dc}{cdt} = 1.048 \times 10^{10}\, Q_1e^{-\frac{Q_1}{RT}}$$

or

$$\log k_1 = 10.0203 + \log Q_1 = \frac{Q_1}{4.571T} \tag{28}$$

The velocity of the reaction

$$PH_3 = P + \frac{3}{2} H_2$$

has been studied by Trautz and Brandharkar [14] and the reaction rate has been shown by them to be free of catalytic effects which might be produced by the walls of the vessel. The observed and calculated values are shown in Table IV. Under k_1 (obs.) are the values taken from the data of Trautz and Brandharkar. Under k_1 (graph) are the values read off the smooth plot of the velocity constants against the absolute temperature. Q_1 (calc.) was computed by means of equation (28), and k_1 (calc.) was obtained by means of the same equation from the mean value of Q_1 or 72,500 cals.

TABLE IV.

T.	$10^3 k_1$ (obs.)	$10^3 k_1$ (graph)	Q_1 (calc.)	$10^3 k_1$ (calc.)
956	22; 11; 22	18.3	72,760	17.5
953	15; 11	15.0	72,740	15.2
948	17; 10; 10; 11	12.0	72,710	12.4
945	8.5	10.2	72,760	10.8
942	17	9.1	72,780	9.6
940	13; 14	8.3	72,740	8.9
936	2.7; 3; 8.3; 7.6; 8.7	7.1	72,730	7.6
933	12	6.3	72,690	6.6
929	5.6	5.5	72,610	5.6
923	4.4	4.6	72,560	4.4
918	3.6	3.8	72,520	3.5
845	0.54		69,920	0.113
785	0.0021			0.0041
719	0.00081			0.000055

The constancy of Q_1 (calc.), and the agreement between the calculated values of k_1 and the values read off the plot afford an interesting confirmation of Dushman's contentions.

In the remainder of Dushman's paper, the same method has been applied in calculating bimolecular velocity constants and also equilibrium constants of various reactions. The agreement between the observed and calculated values is indeed remarkable, but further discussion at this point would be beyond the scope of the present survey.

[14] *Zeits. anorg. Chem.*, 106, 45 (1919).

(10) GENERAL CONSIDERATIONS AND CONCLUSION.

The present brief presentation of the hypothesis which makes radiation the cause of chemical reactivity by virtue of the power of radiation to bring molecules or atoms into an active state makes no pretention of being consistent throughout. There are important differences in the theories of those who have contributed to this field. However, all are agreed that the bath of radiation in which the reacting substances are placed is of fundamental importance in the mechanism of chemical reactions.

Lewis and Perrin have based their theory on the assumption that the energy activation is due to the absorption of radiation of a narrow range of frequencies. For thermal reactions, these frequencies occur in the infra-red region. Langmuir [15] has raised two important objections to this point of view. Firstly, since the reacting substance must absorb radiation of a given frequency, the substance should exhibit an absorption band corresponding to that frequency. He points out that in numerous cases there is no evidence of such bands. Secondly, the energy necessary to activate phosphine at 948° C. is 4×10^{10} greater than can be obtained from the radiation (frequency $392\mu\mu$; calculated by the radiation hypothesis as the frequency of activation of phosphine) of a black body at that temperature.

Lewis and McKeown [16] have attempted to answer these criticisms. They emphasize the important difference between a true photochemical reaction and a thermal reaction. In a photochemical reaction, the temperature of the reacting system is very different from that of the radiation, while in thermal reactions, there is thermal equilibrium between the radiation and the reacting system. Thus, in the latter case, when energy corresponding to a narrow range of frequencies is removed by the reacting system from the bath of radiation, thus disturbing the equilibrium, the bath will tend to restore equilibrium (if maintained at a constant temperature), and more modes of vibration of the required frequency will be produced, thus supplying the necessary energy.

Tolman, by adopting the fundamental different point of view that for thermal reactions all frequencies may stimulate the reacting system, offers another method by means of which Langmuir's objections may be removed. Certainly, not enough data have been

[15] *Jour. Amer. Chem. Soc.*, **42**, 2190 (1920).
[16] *Jour. Amer. Chem. Soc.*, **43**, 1288 (1921).

accumulated to definitely settle whether a narrow band, all frequencies, or all frequencies beyond a threshold frequency are responsible for thermal reactivity.

The radiation theory at present marks the beginning of a new interpretation of chemical reactivity, and should be considered as a step towards the solution of this different problem, not a valid solution. The spirit of approach may best be realized by a quotation from Perrin, who is one of the masters in this field. "J'ai tenté de montrer qu'on développer une theorie cohérente qui voit dans la lumière la cause des reactions chimiques, et qui élucide et rapproche des classes étendues de phénoménes au premier abord assez dissemblables. Dissociations ou combinaisons, phosphorescences, radioactivité, changements d'état physiques, semblent obéir à une même loi fundamental par où se traduit, à notre echelle, la physique intérieure à l'atome. Je ne me dissimule ni la charactère préliminaire d'une étude qui n'est encore que grossièrement approchée ni les incertitudes ou les difficultés qui subsistent, et surtout je sais la necessité de faire des experiences dont certaines sont suggérées avec evidence. Mais le travail sera peut-être considerable et j'ai cru pouvoir indiquer les principes qui le dirigeront."

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[2] BODENSTEIN and DUX: *Zeits. physik. Chem.*, 1913, **85**, 297
[3] NERNST: *Zeits. Elektrochemie*, 1918, **24**, 335.
[4] PUSCH: *Zeits. Elektrochemie*, 1918, **24**, 336.
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On Some Alpha Ray Tracks. C. T. R. WILSON. (*Proc. Cambridge Phil. Soc.*, vol. xxi, part iv.)—Four splendid photographs are reproduced of the tracks of alpha rays from thorium or one of its descendants. It is remarkable how Mr. Wilson can explain just how the idiosyncrasies of the paths came about. His is a powerful method. G. F. S.

THE MODIFICATION OF WIND-TUNNEL RESULTS BY THE WIND-TUNNEL DIMENSIONS.*

BY

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SUMMARY.

THE necessary corrections are determined for the influence of the dimensions of the wind-tunnel upon the results of tests on wings and propellers.

Tests for the investigation of this question have probably been made in every wind-tunnel. The problem is indeed of great importance, whether the influence of the boundaries of the air current can be neglected or not. In the former case the investigator should, whenever possible, clearly and distinctly realize how much he neglects. The application of a correction, on the other hand, enables him to compete successfully with a tunnel of much larger dimensions, where the models have to be kept smaller than is really necessary because the testing engineer is ignorant of the necessary corrections. Here it becomes manifest that an able and well-informed engineer is able not only to increase the efficiency of his wind-tunnel in general, by selecting, arranging and interpreting the tests, but even to increase the effective capacity of his tunnel.

The question of the influence of the dimensions of the wind-tunnel is by no means difficult. I hope that this note will enable every wind-tunnel engineer to become sufficiently acquainted with the present state of this part of aerodynamics. There is a primary and a secondary effect. The theoretical flow of a perfect fluid inside a tunnel does not agree exactly with that in an unlimited space. The difference gives rise to a change of the pressures and of the air forces. In addition it gives rise to a change of the modifications of the theoretical flow caused by viscosity. This again changes the pressures and forces. Only on the former

* Communicated by Dr. Joseph S. Ames, Director, Office of Aeronautical Intelligence, National Advisory Committee for Aeronautics and Associate Editor of this JOURNAL.

influence is exact information available at present. This influence is by far the more important one in most cases.

The modification of the results depends entirely on the type of tunnel, whether (*a*) the air current flows within a tube in contact all around with the solid walls thereof, or whether (*b*) the air current in the zone of testing is a free jet, in direct contact all around with air virtually at rest. The solid wall restricts the free motion of the adjacent particles of air, reacting with such force as to constrain them to flow parallel to its surface, so that the velocity component at right angles to the wall is always zero. The motion of the free jet, on the contrary, is not directly restricted, the surrounding air allowing any shape of the jet. The surrounding air, however, being at rest, exerts the same pressure along the entire surface of the jet. Hence the motion inside the jet is determined by the condition that the pressure on the surface becomes constant.

WING TESTS.

For each of these two wind-tunnel types, the chief kinds of experiments have to be investigated separately. The correction for wing tests in both kinds of tunnels has been given in a complete and correct form by L. Prandtl.[1] I am afraid, however, that his arguments, though absolutely clear and convincing to every mathematician, will not be understood readily by many of his readers who are less mathematically trained. I proceed therefore to repeat the arguments in a much simplified way, making no use of any vortices, but only of the chief characteristics of each aerodynamic flow, *viz.*, its momentum and its kinetic energy.

A wing moved through air produces a distribution of velocities having components in all directions. The investigation is simplified by considering separately the structure of the flow near the wing and the general characteristics of the entire flow. With respect to the flow near the wings it can be assumed that the velocities have no transverse components, *i.e.*, parallel to the span of the wing, so that each longitudinal vertical layer of air remains plane. With respect to the general characteristics of the flow, on the contrary, it can be assumed that the flow has no longitudinal component, so that all transverse vertical layers of air remain plane. The superposition of these two flows gives the final result with sufficient accuracy.

The flow surrounding the wing can not be directly influenced by the walls of the tunnel. The change of this flow is indirectly brought about by the change of the general characteristics of the flow. Hence the present investigation has as its object the two-dimensional distribution of flow in the transverse vertical layers. Each particle of air in the layer is supposed to have originally no velocity components at all parallel to its plane. When approaching, passing and leaving the wing behind it, a transverse two-dimensional distribution of flow is gradually built up in each layer. The momentum of the air downward transferred to the layer with the thickness equal to the velocity V is equal to the lift L. The kinetic energy of the flow in this layer when finally built up depends on the longitudinal projection of the wing or wings and on the distribution of the lift over the wings. It may be denoted by P. This kinetic energy can be assumed to be concentrated in a fictitious quantity of air $K\rho V$, moving with constant downward velocity u and having the momentum L received from the wing. It will be noticed that K has here the dimension of an area, the area of the apparent mass of the front view of the wing. The induced drag has to absorb the energy P necessary to create the flow. This is expressed by the equations,

$$P = KV\rho\frac{u^2}{2} \qquad L = KV\rho u$$

Therefore

$$D_i = \frac{P}{V} = \frac{L^2}{4V^2\frac{\rho}{2}K}$$

The resultant air force has the average inclination towards the vertical

$$\alpha_i = \frac{D_i}{L} = \frac{L}{4V^2\frac{\rho}{2}K}$$

These conclusions remain correct whether the air current is unlimited or bounded by the walls of the wind-tunnel. In the latter case, however, the transverse flow is modified and hence its apparent area of mass K, too. The problem is thus reduced to the determination of the apparent mass K' inside a tunnel, if the apparent mass K under the same conditions in unlimited air is known.

The exact solution depends not only on the area of the apparent mass, K, but on the exact distribution of the lift and on the shape of the wind-tunnel section. For the present purpose, however, it is exact enough to solve the problem for one particular condition, chosen so as to make the solution as simple as possible, and to assume that the result holds good for any other case with equal area K and area S' of the wind-tunnel section. The particular problem, easy to be computed, is an arrangement of wings like Venetian blinds, a multiplane, as it were, of an infinite number of wings, in front view in the form of a circle, and with such distribution of lift as to produce a constant induced angle of attack. The diameter of the circle containing the wings may be d, the cross-section of the tunnel may be circular, concentric to the wing and having the diameter D. The final two-dimensional flow is determined by its radial velocity components at the points of the inner and outer circle. The latter is at rest, hence the radial velocity at its points is zero. The inner circle moves with the velocity v, hence the radial velocity component at its points is $v \sin \varphi$, where φ denotes the angle between the radius of the point and the diameter at right angle to the motion v. Let r denote the distance of any point from the centre. Then the flow under consideration has the velocity potential

$$P = -u \sin \varphi \left(r \frac{d^2}{D^2 - d^2} + \frac{1}{4r} \frac{d^2 D^2}{D^2 - d^2} \right) \tag{1}$$

I prove this by forming the expression for the radial velocity component dP/dr

$$\frac{dP}{dr} = -u \sin \varphi \left(\frac{d^2}{D^2 - d^2} - \frac{1}{4r^2} \frac{d^2 D^2}{D^2 - d^2} \right) \tag{2}$$

Consider first the outer circle, and accordingly substitute in equation (2) $\frac{1}{2}D$ for r. This substitution gives indeed

$$\frac{dP}{dr} = 0$$

At the points of the inner circle, on the other hand, $r = \frac{1}{2}d$. This substituted in equation (2) gives

$$\frac{dP}{dr} = u \sin \varphi$$

and thus the boundary conditions for the flow are shown to be fulfilled. It complies in addition with the general, Laplace's, condition for the potential flow of a perfect fluid.

The same substitution in the expression for the potential (1) gives the potential at the points of the inner circle

$$P = -u \sin\varphi \frac{d}{2} \frac{D^2 + d^2}{D^2 - d^2} \tag{3}$$

The kinetic energy of this flow has now to be determined. Since no fluid passes through the outer circle, this is done by integrating along the inner circle alone. The kinetic energy of the flow is in general

$$\frac{\rho}{2} \int P \frac{dP}{dn} ds \tag{4}$$

the integral to be taken along all boundaries. Herein, ρ denotes the density of the fluid, P the potential, dP/dn the velocity component normal to the boundary and ds the length of an element of the boundary. In this case, the element of the boundary has the magnitude

$$ds = \frac{1}{2} d\, d\varphi \tag{5}$$

The radial component of the velocity was $u \sin\varphi$. The potential was given in equation (3). Hence the integral assumes the form

$$\frac{\rho}{2} \int_0^{2\pi} \left(\frac{d}{2}\right)^2 \frac{D^2 + d^2}{D^2 - d^2} u^2 \sin^2\varphi\, d\varphi \tag{6}$$

and the kinetic energy results to be

$$\frac{\rho}{2} d^2 \frac{\pi}{4} u^2 \frac{D^2 + d^2}{D^2 - d^2} \tag{7}$$

corresponding to the apparent additional mass of the circle

$$d^2 \frac{\pi}{4} \frac{D^2 + d^2}{D^2 - d^2}$$

or approximately

$$d^2 \frac{\pi}{4} \left(1 + \frac{2d^2}{D^2}\right)$$

The entire apparent mass of the flow, including the fluid inside the inner circle, moving with constant velocity, is therefore

$$2d^2 \frac{\pi}{4} \left(1 + \frac{d^2}{D^2}\right)$$

Introducing now K, the area of apparent mass of the wings in an unlimited flow, that is, in this case $K = 2d^2 \frac{\pi}{4}$, and S', the cross-section of the air current, in this case $D^2 \frac{\pi}{4}$, and expressing

d and D by means of K and S', it results that the apparent mass of the wing is increased in the ratio

$$1 + \frac{1}{2} K/S'$$

The induced angle of attack and the induced drag are inversely proportional to this apparent mass. It follows therefore that in a tunnel with the cross-section area S' the induced angle of attack and the induced drag are decreased in the ratio

$$\frac{1}{1 + \frac{K}{2S'}}$$

For a single wing in particular the area K is $b^2 \frac{\pi}{4}$ where b denotes the span. Hence then the induced drag and angle of attack observed in the closed wind-tunnel are smaller than the corresponding quantities would be in a tunnel of infinitely large dimensions and are decreased in the ratio

$$\frac{1}{1 + \frac{b^2}{2D^2}}$$

I proceed now to the free jet. That flow is produced by pressures over the wings only; there is no pressure difference at the boundary of the jet. Hence the potential over the boundary, essentially identical with the impulsive pressure creating the flow, is zero. The same method as before gives almost the same flow as before, only the sign of the second term of the potential P is reversed. Hence the induced angle of attack and the induced lift are now increased in the same ratio

$$1 + K/2S'$$

for any wing and in the ratio

$$1 + b^2/2D^2$$

for a single wing with the span b.

PROPELLER TESTS IN CLOSED TUNNEL.

The influence of the wind-tunnel walls on the result of propeller tests has been theoretically investigated by R. M. Wood.[2] The results are not quite as completely and clearly brought out as Doctor Prandtl's. They seem to be disfigured by some misprints, and I am unable to bring the result as given analytically in agreement with his diagram.

Mr. Wood substitutes an ideal propeller with constant density of thrust per unit of propeller disc area and without torque for the actual propeller. I follow him herein. The air is now accelerated in direction of its original motion. Therefore the momentum is not distributed over the entire air, but remains concentrated in the air passed through the propeller disc. When passing the propeller disc it has already received half the increase of velocity. Let the velocity of flight be V and the final velocity of the slip stream be v. The velocity with which the air passes through the propeller disc is then $V + \frac{v}{2}$ (relative to the propeller) and hence the mass of air passing it per unit time is $S(V + \frac{1}{2}v)\rho$, where S denotes the propeller disc area, $D^2 \frac{\pi}{4}$ and ρ the density of air. The final increase of momentum per unit of time, equal to the thrust is $T = Sv(V + \frac{1}{2}v)\rho$. This gives a quadratic equation for v. Let C_T be

$$C_T = \frac{T}{SV^2 \frac{\rho}{2}}$$

then the equation gives

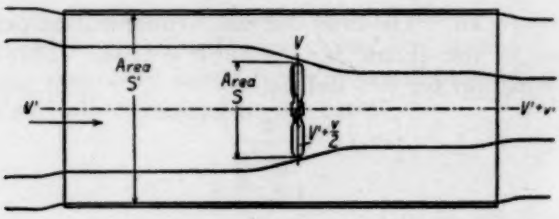
$$v/V = \sqrt{1 + C_T} - 1 \sim \frac{1}{2} C_T,$$

if C_T is very small.

In many practical cases C_T is not small enough for the use of the approximate expression. Suppose now the propeller to be surrounded by a coaxial cylindrical tube representing the tunnel as shown in Fig. 1. The length of the tube is supposed to be large, but still finite, so that in front of it and behind it the flow occupies the entire space. This tube in addition is supposed to transfer no momentum to the fluid. Its wall being parallel to the motion in all points, this is almost a matter of course. The ends, however, in this hypothetical case of a perfect fluid, even when infinitely thin, are able to transfer finite longitudinal forces since the velocity near the edges and hence the pressures may become infinite. It is supposed that these forces acting on the edges neutralize each other. This requires equal edge velocities at the entrance and at the outlet, and this again requires, approximately at least, equal velocity differences inside and outside the tube at both its ends.

The tube transferring no momentum to the fluid, the arguments used before for the propeller in the unrestricted air remain entirely unchanged. The original velocity V' in the unrestricted space, the slip stream velocity v, and velocity with which the air passes the propeller and the propeller forces are exactly the same as before. The whole configuration of the flow, however, has been changed. The original and the final velocity occur only outside of the tube and hence are farther removed from the propeller. Inside the tube these velocities cannot be found. The longer the tube is, the longer is the path at the points of which the air has already begun to change its velocity, but has not yet

FIG. 1.



Slip stream transfigured by a tube.

attained to its final velocity. This not only refers to the air passing through the propeller disc and receiving momentum, but also to the air inside the tube surrounding the slip stream. This air has a velocity inside the tube different from the original and final velocity. If the tube is long enough, the flow in front of and behind the propeller attains to steady conditions, flowing with constant velocity and pressure parallel to the axis. Neither this velocity nor that of the slip stream inside the tube agree, however, with the final velocities.

The portion of the configuration of flow outside the tube is only fictitious and does not exist with an actual wind-tunnel. The problem therefore arises to determine the original velocity V' from the observed data of the test, since this velocity V' corresponds to the velocity of flight under which the propeller is supposed to work. The area of the propeller disc S and the cross-section of the wind-tunnel S' and the thrust T are supposed to be determined. In addition the velocity of the flow must have been measured at one point at least. It is most convenient to

determine it far in front of the propeller, as there the flow is smooth and not disturbed. The velocity there may be denoted by V. In the plane of the propeller disc, outside of it, the remaining cross-section is narrow and the measurement of the velocity difficult, this the more so, as the propeller is not an ideal one and the velocity in this cross-section hardly quite constant and without fluctuations. I assume now that the change of all velocities brought about by the walls of the tunnel is small when compared with these velocities themselves. The change of the slip stream contraction is then small, too, when compared with the contraction itself. This assumption leads to results exact enough for the practical application. In addition this proceeding can be considered as the first step to a more exact computation. From this assumption, it follows that the air inside the tunnel, *not* passing through the propeller disc, flows through the cross-sections

(a) far in front of the propeller: $S' - S\left(1 + \frac{v}{2V}\right)$

(b) in the plane of the propeller: $S' - S$

(c) far behind the propeller: $S' - S\left(1 - \frac{v}{2V}\right)$

Its average velocity (b) in the propeller plane being denoted by W, the velocity in front of and behind the propeller would result

$$W_{(a)} = W_{(b)} \frac{S' - S}{S' - S\left(1 + \frac{v}{2V}\right)}; \quad W_{(c)} = W_{(b)} \frac{S' - S}{S' - S\left(1 - \frac{v}{2V}\right)}$$

Outside the tube the velocity is V'. But as demonstrated before, the velocity difference inside and outside the tube is equal at both ends. This gives the condition

$$W_{(b)} = V'$$

since $\frac{v}{2V}$ is a small quantity and it appears the simple result:

The average velocity in the propeller plane outside the propeller disc agrees with the fictitious velocity of flight.

The problem would thus be solved in the simplest way. But as mentioned before, it is not always practical to measure the velocity very near to the propeller. It remains therefore to find a simple relation between the fictitious velocity of flight V' and the velocity V far in front of the propeller. That is now easy

enough. The velocities V and V' are inverse as their cross-sections $S' - S\left(1 + \frac{v}{2V}\right)$ and $S' - S$, hence

$$V' = V \frac{S' - S}{S' - S\left(1 + \frac{v}{2V}\right)} \sim V\left(1 + \frac{v}{2V} \frac{S}{S' - S}\right) \sim V\left(1 + \frac{v}{2V} \frac{S}{S'}\right)$$

or the magnitude of v substituted

$$V' \sim V\left(1 + \frac{1}{2}(\sqrt{1 + C_T} - 1) \frac{S}{S'}\right)$$

That is the formula which I wished to obtain. For very small values of C_T it becomes

$$V' \sim V\left(1 + \frac{C_T}{4} \frac{S}{S'}\right)$$

but in practice C_T is often not small enough for the application of this simplified formula.

Mr. Wood obtains the final approximate formula

$$1 - \frac{V'}{V} = 55 X^2 \frac{T}{\rho a_3 V^2}$$

where a_3 denotes the cross-section of the slip stream and X its ratio to the cross-section of the wind-tunnel. If we assume two misprints and write instead of this formula

$$1 - \frac{V'}{V} = .55 X \frac{T}{\rho a_3 V^2}$$

Mr. Wood's formula almost agrees with the one obtained by myself for small thrust coefficient C_T.

PROPELLER TESTS IN A FREE JET.

With propeller tests in a free jet no correction of the velocity is necessary. The surface of the jet is a surface of constant pressure, hence the cylindrical parts of the flow far in front and far behind the propeller have the same pressure. Therefore the arguments used for the propeller in unrestricted air remain quite unchanged. The velocity far in front of the propeller is directly identical with the fictitious velocity of flight. The contraction of the slip stream remains unchanged too. The exact shape of the slip stream is slightly changed, but this has no noticeable effect on the air forces in general.

WIND-MILL TESTS.

The arguments used for propellers are good for wind mills, too. Wind-mill tests in a free jet are in no need for a correction. The fictitious velocity of flight for wind-mill tests in a closed tunnel with the velocity V far in front of the wind mill is

$$V' = V\left(1 + \frac{v}{2V}\frac{S}{S'}\right)$$

as before.
With wind mills v/V is negative and has the value

$$\frac{v}{V} = 1 - \sqrt{1 + C_T}$$

Hence

$$V' = V\left(1 - \frac{S}{2S'}(\sqrt{1 + C_T} - 1)\right)$$

or approximately for small thrust coefficient C_T.

$$V' = V\left(1 - \frac{C_T}{4}\frac{S}{S'}\right)$$

CONCLUSION.

The investigation thus finished showed that the open jet decreases the angle of attack of a wing and hence its lift, increasing the drag. It has no noticeable effect on the results of the other tests mentioned, unless the models are exceedingly large. The closed tunnel increases the angle of attack of a wing, thus increasing its lift and decreasing its drag. The velocity measured far in front of the model is too large with propeller tests and too small with wind-mill tests. Formulas giving the necessary corrections are given in each single section.

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A Theory of Meteors and the Density and Temperature of the Outer Air to Which it Leads. F. A. LINDEMANN and G. M. B. DOBSON, University of Oxford. (*Proc. Roy. Soc.*, A 717.)—"A meteor is an extra-terrestrial particle which enters the air at high speed, it becomes visible (owing to collision of the fast vapour molecules with air molecules) when its surface becomes hot enough to

evaporate appreciably, and it disappears when it has evaporated practically completely." "All meteors move at a speed great compared to the velocity of sound." The meteor strikes the earth's atmospheric envelope and upon reaching air of a certain density it forms in front of it a cap of condensed air, heated adiabatically by the compression. There is an influx of heat from this cap to the material of the meteor whose temperature rises until vapor is given off.

The authors show that it is possible to give equations connecting the various quantities concerned in the result and that these equations are not so replete in inaccessible quantities that no definite deductions can be drawn. On the contrary quite definite and astonishing conclusions are reached when the equations are applied to the observed data of meteors. "The heights, paths and velocities of some thousands of meteors have been observed. They appear, in general, at heights between $1.6.10^7$ and 7.10^6 cm., and disappear at heights below $1.2.10^7$ cm., mostly at about 8.10^6, though some, of course (the so-called meteorites) reach the ground. Velocities from $9.5.10^5$ to $1.6.10^7$ cm./sec. have been recorded."

The mass of a meteor can be computed from the equations. A meteor traversing a distance of 6.10^6 cm. in 1.5 seconds, "and appearing at a distance of $1.5.10^7$ cm. as bright as a first-magnitude star" will have a mass of $6.25.10^{-3}$ gram. If it is made of iron, its diameter is one-ninth cm.

The most surprising deductions are those relating to the temperature and density of the air at high altitudes. "Some thirty years ago Teisserenc de Bort announced the discovery that the temperature gradient in the atmosphere, which amounts to some $6.5.10^{-3}$ degree/cm. for the first 10 km., becomes negligibly small at greater heights. Since this time it has become usual to treat the temperature as constant for all heights above this limit, and various detailed numerical estimates, extending to heights of hundreds of kilometres, have been published, which are based on this assumption. So far, however, no evidence for it has been adduced beyond the 'ballon sonde' observations, which scarcely extend above 25 km." It is shown "that existing observations enable us to say with considerable certainty that the density at heights above 65 km. is very much higher than is commonly supposed, and that the temperature must increase from its value of something like 220° abs. at heights between 12 and 50 km. to something like 300° abs. at those heights." This difference of density is no small matter for at 150 km. it is calculated to be 1000 times as great as it has been believed to be. The higher temperature at great heights is explained by the importance of ozone in the outer portions of the atmosphere. These new results will need to be regarded in forming theories of the aurora, for at the lower limit of this the density now comes out 100 times as great as it was held to be.

G. F. S.

AN IMPULSE ELECTRIC MOTOR FOR DRIVING RECORDING INSTRUMENTS.*

BY

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SUMMARY.

THE chief purpose in undertaking the development of this synchronous motor was the creation of a very small, compact power source, capable of driving the film drums of the recording aircraft instruments designed by the staff of the National Advisory Committee for Aeronautics.

The working parts of the motor are few and simple. They consist of four spool type field coils, a reciprocating armature, a ratchet wheel and two pawls. The field coils, operating in pairs, alternately pull the armature from one pair of pole faces to the other pair. This reciprocating motion is transmitted to the ratchet wheel through the two pawls, motion in either direction producing a positive advance of the wheel. Rotation of a very regular character is thus secured.

The motor is 1⅜ inches long, $1\frac{3}{16}$ inches wide and ⅞ inch high, with a volume of 1.43 cubic inches, and a weight of .165 pound (75 gms.). It produces approximately 6.0×10^{-5} H.P., with an efficiency of 1.0 per cent. The speed range is from 0 to 35 R.P.M., the torque being .234 pound-inch (269.6 g.-cm.) at the lower speeds with 8 volts applied.

Due to its small size and light weight, its inherent slow speed and property of absolute synchronization, the motor is particularly well adapted to aircraft instrument work. Application of this type of power source may also be made to automatic recording instruments of all kinds, to indicating devices requiring absolute precision of movement, and to remote control work.

* Communicated by Dr. Joseph S. Ames, Director, Office of Aeronautical Intelligence, National Advisory Committee for Aeronautics and Associate Editor of this JOURNAL.

INTRODUCTION.

The specific problem which was responsible for the development of this direct current synchronous motor, was that of driving the film drum of an instrument called the sun kymograph.

The requirements of this instrument are four-fold: First, the drive must be slow speed; second, the rotation must be uniform and regular; third, the part of the drive attached to the instrument must be small, compact and light in weight; and fourth, the connecting link between the instrument and airplane must be flexible.

To meet these requirements three forms of mechanical drives, and two types of small electric motors were investigated and tried.

METHODS AND APPARATUS.

The mechanical drives investigated consisted of flexible cables which received their power from a constant speed motor mounted on the floor of the airplane. These cables drove the kymograph film drum through a small clutch attached to the instrument.

The three forms consisted, first, of a solid wire enclosed in a flexible housing; second, of a standard Van Sicklen tachometer cable and housing, and third, of a double opposed spring cable (Van Sicklen), without a housing, but guided at intervals by rings.

The results obtained with these drives were unsatisfactory. Due to the slow speed required, which caused a spasmodic sticking and releasing of the cable within its housing or guiding rings, all three types imparted a very irregular rotation to the film drum. The flexibility of these drives was also inadequate for the work involved.

The first type of electric drive investigated was a low-frequency alternating-current motor. This was built very much like a standard direct-current telephone relay. It depended for its action on the cyclic attraction of a small laminated bar armature to and from a pair of spool type coil magnets. A spring pawl transmitted the reciprocating motion of the armature to a ratchet wheel.

A second form of alternating current motor, similar in construction and principle to the polarized relay or the alternating current bell ringer, was also investigated. As in the first form of this type of motor, a pawl transmitted the oscillating motion of the armature to a ratchet wheel.

Both of these motors operated fairly well with very light loads. But a load equal to that of a film drum retarded the armature sufficiently to destroy the synchronism between armature and magnetic flux.

In the second form of motor, it was particularly noticed that the frequency of the alternating current had to coincide exactly with the natural period of the oscillating parts for the motor to function. Also the starting torque of the motor was very low, and the efficiency of both motors was less than one-twenty-fifth of one per cent. Hence these two electric drives were also inadequate and unsatisfactory.

The second and successful type of electric drive investigated was built much like a standard telephone relay, but had double opposed electromagnets. These alternately pulled the armature from one pair of pole faces to the other. This reciprocating motion was transmitted to the ratchet wheel through a pawl, power being directly imparted in only one direction.

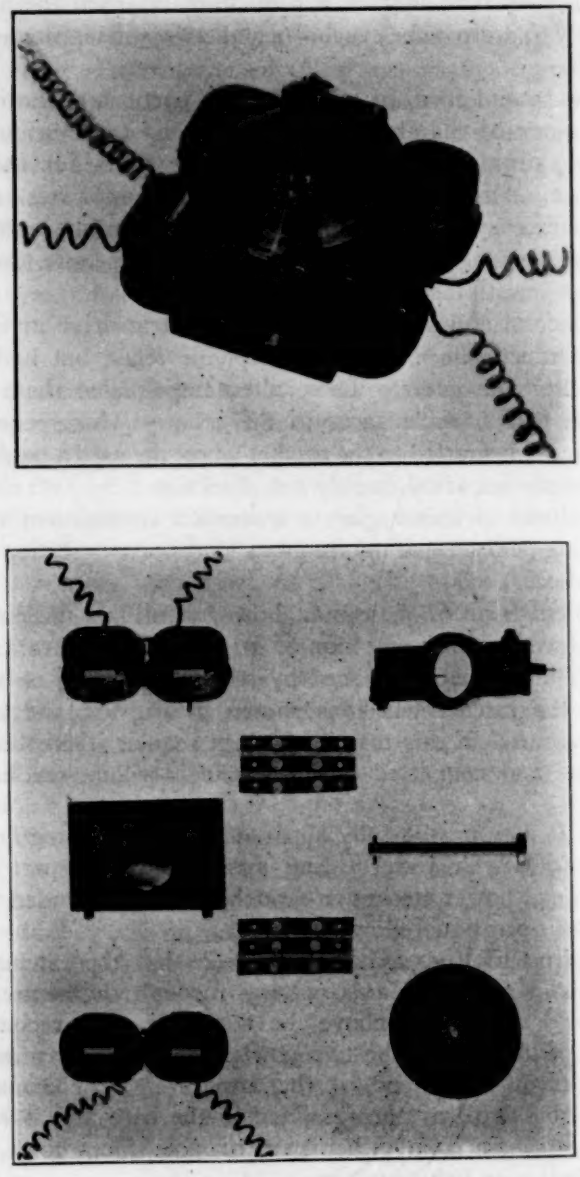
This form of motor gave a somewhat intermittent rotation, there being sixty separate impulses for one revolution of the ratchet wheel.

The final form of the motor, however, utilizes the motion of the armature in either direction to give a positive advance to the wheel. This was accomplished by two pawls acting on opposite sides of the ratchet wheel as shown in Figs. 1 and 2. The rotation secured in this manner is very regular, there being 480 continuous and connected power strokes for one revolution of the wheel.

Since it may not be fully apparent, from the foregoing brief description, how a reciprocating armature can impart definite unidirectional power strokes to a ratchet wheel a detailed description of the operation follows.

Referring to Fig. 2, it will be seen that the ratchet wheel rotates about a vertical axis passing through the centre of the motor; also that it lies above the field poles and reciprocating armature, and between the two pawls, which latter are mounted in brackets at either end of the armature. The armature is supported by two leaf springs fixed in the base and is returned by these springs from either pair of pole faces to a neutral position half-way between them.

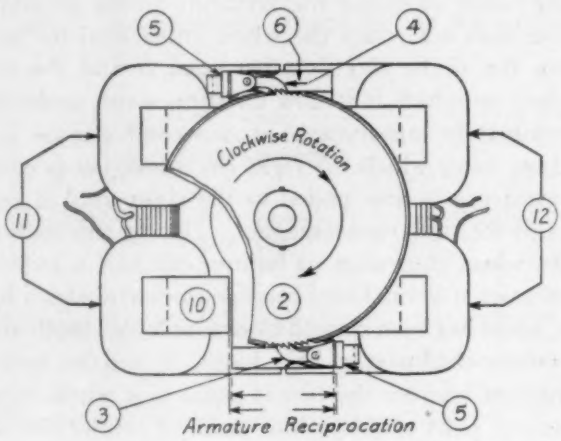
FIG. 1.

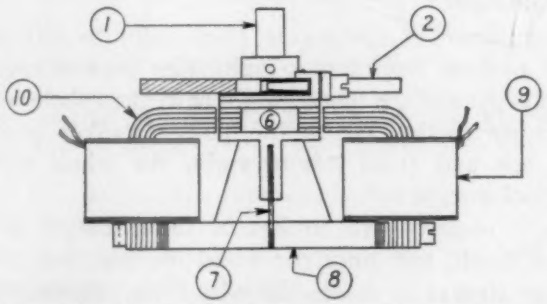


Direct current synchronous motor and parts.

The moving parts of the motor consist of the armature, the two pawls and the ratchet wheel. There are no connecting rods or bell cranks.

FIG. 2.





Diagrammatic drawing of direct current synchronous motor.

1, vertical shaft; 2, ratchet wheel; 3, pawl *A*; 4, pawl *B*; 5, pawl brackets; 6, armature; 7, armature springs; 8, base; 9, field coils; 10, field poles; 11, left electromagnet; 12, right electromagnet.

Assuming now the left electromagnet to be energized, the action from the neutral position is as follows:

The armature is pulled to the left until it reaches the pole faces of the left electromagnet. During this motion, pawl *A* has rotated the wheel clockwise one-quarter of a tooth. At the same time pawl *B* has ratcheted back in a counter-clockwise direction

one-quarter of a tooth and has dropped into position behind the tooth over which it has just moved. The armature is now in position for a complete power stroke from left to right.

Assuming the left electromagnet to be de-energized, the armature springs start to return the armature to the neutral position. This action does not rotate the wheel under load but serves only to take up the slight play between pawl *B* and the three teeth of the wheel on which it is now exerting some pressure.

Approximately one-sixtieth of a second elapses during the above action, after which the right electromagnet is energized.

The armature is now pulled to the right until it reaches the pole faces of the right electromagnet. During this motion pawl *B* rotates the wheel clockwise, as before, one-half a tooth. At the same time pawl *A* is ratcheted counter-clockwise also a half tooth. Since the wheel has been rotated clockwise a half tooth and pawl *A* moved counter-clockwise a half tooth, it will be seen that the relative motion between the two is equal to a whole tooth.

Therefore, pawl *A* drops into position behind the tooth over which it has just moved. Thus the power stroke has been completed and the armature brought into position for the following stroke from right to left.

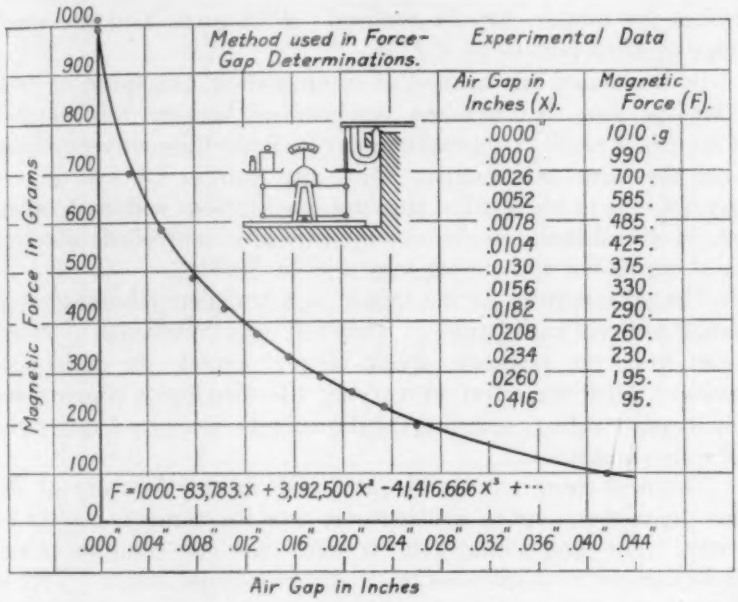
The sequence of operations from right to left are exactly the same as those from left to right with the one exception that pawl *A* now rotates the wheel, while pawl *B* ratchets into position over another tooth. Hence the power strokes proceed from right to left and from left to right, the wheel always being rotated clockwise.

Since it requires two strokes of the armature to move the wheel one tooth, and since the wheel has 240 teeth, it requires 480 power strokes to rotate the wheel one complete revolution. Hence the inherent slow speed of the motor.

The maximum air gap required in this motor between the armature and either pair of pole faces is very small, actually about .008 inch. This gap varies in operation from .008 inch to zero, so that the average gap is only .004 inch. Hence the efficiency of the magnetic circuit is high. This is accomplished by using ratchet teeth of small pitch, and by the fact that a complete power stroke requires an air gap of only one-half the tooth pitch.

Referring to Fig. 3 it will be seen that the magnetic pull between two plane surfaces which are separated by small air gaps is neither inversely proportional to the gap nor to the square of the gap, but follows a law of the following form: $F = C - C_1X + C_2X^2 - C_3X^3 +$. In this equation F is the magnetic force or pull; C, C_1, C_2 and C_3 are constants determined by the size and shape

FIG. 3.



Magnetic force variation for small air gaps.

of the poles faces and by the total magnetic flux; and X is the gap between magnet and armature.

It was found that the magnetic pull in this motor at zero gap was 1150 grams (2.54 lbs.) and at .008 inch gap, 550 grams (1.21 lbs.). The armature springs therefore were designed to equalize this varying magnetic force so as to give a pull of 850 grams (1.87 lbs.) throughout the whole power stroke. Thus the springs store 3.05 cm.-g. (.00264 in.-lb.) of energy during the last half of each power stroke and return it during the first half of the following power stroke.

The alternate energizing and de-energizing of the left and

right electromagnets is accomplished by a distributor driven by a constant speed motor in an average case at about 720 R.P.M. This distributor makes and breaks the electric circuit for each electromagnet of the motor once for each revolution. Hence at 720 R.P.M. of the distributor the motor armature has transmitted 1440 power strokes to the ratchet wheel, thus producing a motor speed of three revolutions per minute. This speed is readily controlled so that a range of from zero to 16,800 power strokes per minute may be realized. This gives a motor speed range of from zero to 35 R.P.M.

By the use of this method of commutation, and speed control, it will be seen that absolute synchronism between any number of motors is readily obtained by merely taking their current supply from the same distributor. Thus any number of instruments may not only be operated in absolute synchronism with each other, but, if the distributor be chronometrically controlled, absolute speed regulation and timing may also be realized.

The performance of the motor in a complete laboratory test proved entirely satisfactory. This test was conducted to determine, first, the complete speed range; second, the maximum torques; third, the effect of varying the distributor-commutator time-contact ratios; and fourth, the current consumed under the different conditions.

The time-contact ratio, as here used, means the ratio of the time the motor is cut in circuit to the time the motor is cut out of circuit. The time-contact ratio is taken over two complete power strokes or one revolution of the distributor-commutator. This is also called a cycle and the amount of actual contact is determined by the number of degrees of commutation per cycle.

It will be readily understood that to obtain the best efficiency from the motor, the current supplied through the distributor-commutator should be cut out the instant the armature has completed its power stroke. In order to accomplish this result, without any complication, the correct length of the distributor-commutator segment, which makes and breaks the circuit and thus produces a power stroke, was determined in this test for all speeds and torques.

The data obtained are tabulated in Table I. Curves showing the torques in gram-centimetres, speeds, degrees of commutation, efficiencies, current consumed in amperes, horsepowers and the

TABLE I.

Direct Current Synchronous Motor Performance Data.

Torque in G.-Cm.	Degrees of Commutation per Cycle.													
	45°		90°		135°		180°		225°		270°		315°	
	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.
265.	0	.131	0	.263	0	.394	0	.523	0	.656	0	.788	0	.919
232.6	.....	....	.....	....	.....	....	.....	....	.....	....	5,400	.67	6,600	.69
200.5	1,600	.130	3,200	.24	4,200	.33	5,100	.41	6,000	.49	8,920	.53	10,500	.57
174.6	1,800	.115	4,100	.22	5,140	.30	6,400	.38	7,920	.45	.....	....	.....	....
135.8	2,400	.11	4,900	.19	6,600	.27	8,000	.33	8,800	.41	10,800	.49	12,500	.51
103.5	2,900	.10	5,700	.175	7,800	.24	9,300	.31	11,000	.34	12,000	.42	.....	....
84.1	3,060	.09	6,300	.17	8,700	.23	11,000	.29	.....	....	.....	....	.....	....
64.7	3,500	.08	7,400	.155	9,600	.20	12,400	.25	12,400	.32	13,800	.39	14,800	.42
45.25	.....	....	8,400	.15	10,780	.18	.....	....	.....	....	.....	....	.....	....
32.16	4,800	.075	.....	....	.....	....	.....	....	.....	....	.....	....	.....	....
0.00	7,000	.06	12,400	.10	14,000	.16	15,100	.19	16,200	.23	16,800	.29	17,000	.36

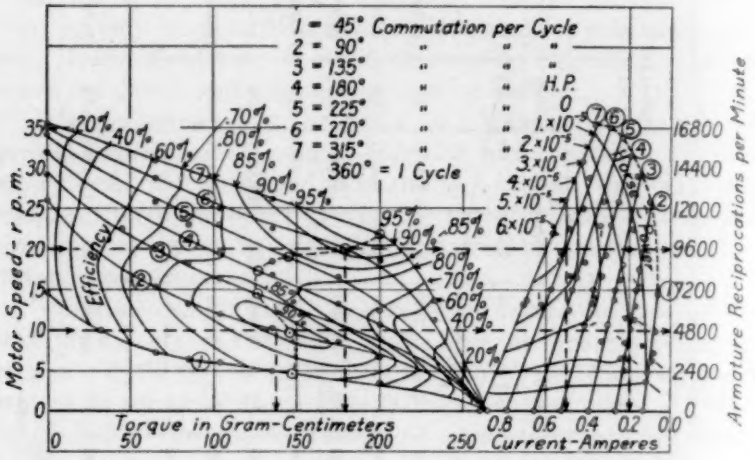
P. S.=Power strokes per minute.
Amp.=Current consumed at 8 volts.

number of armature reciprocations per minute are plotted on curve sheet Fig. 4.

Thus, following the dotted lines, starting at 10 or 20 R.P.M., we may find the other characteristics of the motor for any specific number of degrees of commutation per cycle.

R.P.M.	10	20
Degrees of commutation per cycle	90°	270°
Torque	138	179
Efficiency	0.91%	0.92%
Current amperes	0.20	0.50
Horsepower	1.8×10^{-5}	4.9×10^{-5}
Armature reciprocations per minute	4800	9600

FIG. 4.



Performance chart of type "B" direct current synchronous motor.

RESULTS.

The new type of power source for aircraft instruments has the following specifications:

(1) Size: Length, 1⅜" (3.49 cm.); width, 1³/₁₆" (3.02 cm.); height, ⅞" (2.22 cm.).
(2) Weight: 75 gms.
(3) Speed range: 0 to 35 R.P.M.
(4) Current consumption: 0.1 to 0.9 amperes at 8 volts.
(5) Torque (max.): 269.6 g.-cm.
(6) Power (max.): 6×10^{-5} H.P.
(7) Efficiency (max.): .99 per cent.

As it may be interesting to compare the impulse motor with the D.C. governed series motor (Fig. 5) now used in the instruments of the committee, the following table is attached:

FIG. 5.

D.C. governed series motor.

Size: 2.5" (6.35 cm.) × 2.5" (6.35 cm.) × 4.2" (10.67 cm.).
Weight: 750 gms.
Speed range: 500–2500 R.P.M.
Current consumption: Normal, 1.75 amps. at 8 volts.
Current consumption: Starting, 10.5 amps. at 8 volts.
Power (max.) at 1080 R.P.M. = .0051 H.P.
Power (max.) at 1790 R.P.M. = .0054 H.P.
Efficiency at 1080 R.P.M. = 12.7 per cent.
Efficiency at 1790 R.P.M. = 18.8 per cent.
Torque required to turn standard film drum with no reduction gearing varies from 27 g.-cm. to 270 g.-cm.
Efficiency of combined system of this type of motor and gearing when driving a good drum = .007 per cent.

The advantages of the impulse type of motor for instrument work are:

(1) Size and shape permit easy installation in the instrument base, thus providing space for additional apparatus, or making possible a material reduction in the size of the instrument. Its volume is 1.43 cubic inches.

(2) Light weight.

(3) Inherent low speed.

(4) Low current consumption, thus decreasing the number of storage batteries necessary for average flight work to approximately 40 per cent. of the present requirement.

(5) Constant torque at the speed range used.

(6) High efficiency for its size.

(7) Absolute synchronism or zero speed variation between any number of like motors.

(8) Normal speed instantaneously on closing the switch.

(9) Dead stop instantaneously on opening the switch.

(10) Remote control of speed of all motors in operation from the distributing source.

(11) Long life due to low-bearing pressures. (1) Pawl-bearing pressure 300 lbs./sq. in. (2) Main-bearing pressure 12 lbs./sq. in.

(12) Low construction cost due to: (1) Few parts; (2) spool type coils; (3) elimination of rotating contacts and brushes.

Italy Searching for Oil.—The "Drang nach Osten" was originally a pressure for many commercial advantages, but of late the main object of the great nations in securing opportunities in the East is to control the oil-fields. Great activity is now evident in the exploration of all regions that may yield this liquid, which has become important in peace and war. From a recent issue of the *Bollet. Chimico-Farmaceutico* (1923, lxii, 195) it is learned that Italian authorities are aroused to the necessity of securing oil-fields and have begun experimental borings within their own territory. A committee of geologists has been appointed to conduct the investigations. Some small sources of oil already exist. Apparatus for deep borings was obtained from Germany through the reparations agreement. One boring made in 1921 reached a depth of 479 metres (about 1600 feet) from which a yield of about 200 gallons per day has been obtained. In other regions surface indications of oil and of gas have been detected. A school for instruction in oil exploration has been organized. H. L.

MOTION PICTURE PHOTOGRAPHY FOR THE AMATEUR.*

BY

C. E. K. MEES, D.Sc.

Director, Research Laboratory, Eastman Kodak Company,
Associate Editor, Member of the Institute.

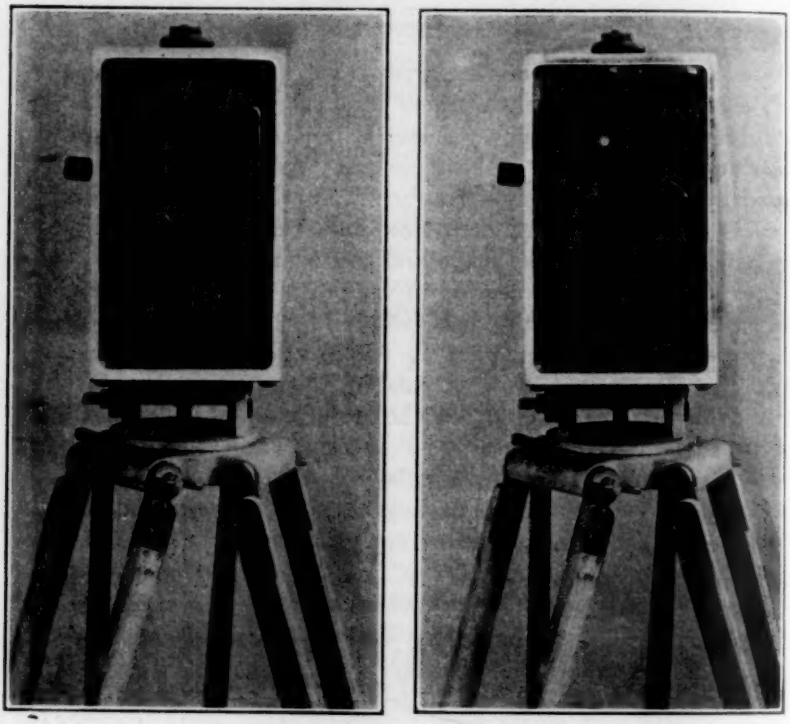
AMATEURS have played a great part in the development of photography. The early workers in photography were naturally amateurs, though the first successful process, that of Daguerre, was utilized chiefly for making portraits and was the process first used by professional photographers. While Daguerre's process was being exploited, however, Fox Talbot discovered his process in which a negative was made and then printed, the practice followed at the present time, and in which the exposure, insufficient to produce a visible image, was followed by development to obtain a negative of sufficient strength for printing. Talbot, in fact, laid the foundations for our modern systems of photography. Scott Archer, the inventor of the wet collodion process, which followed the calotype process of Fox Talbot, and Doctor Maddox, who made the first gelatin emulsion, were both amateurs, and all the early work on dry plates was done by amateurs until about 1880, when the manufacture of dry plates on a commercial scale was fully established.

Important as was the work of amateurs, however, the possibilities of amateur photography were necessarily limited by the very cumbersome equipment which was required for the wet plate process, and even when dry plates became available, the portability of apparatus and the simplicity of photography were very far from their present level. Marked as has been the improvement in apparatus for the utilization of dry plates, the greatest step in the making of photography available to everybody was the development of the film camera by George Eastman.

* Presented at a meeting of the Sections of Physics and Chemistry and Photography and Microscopy of The Franklin Institute held Thursday, February 1, 1923, and published as Communication No. 170 of the Research Laboratory of the Eastman Kodak Company.

The causes that restricted the use of photography by amateurs before the coming of the kodak have operated to limit the use of motion picture photography by other than professional photographers. The apparatus required is very heavy and cumbersome; the standard motion picture camera, tripod, and magazine form a heavy load for one man, and in addition the cost of the film is

FIG. 1.



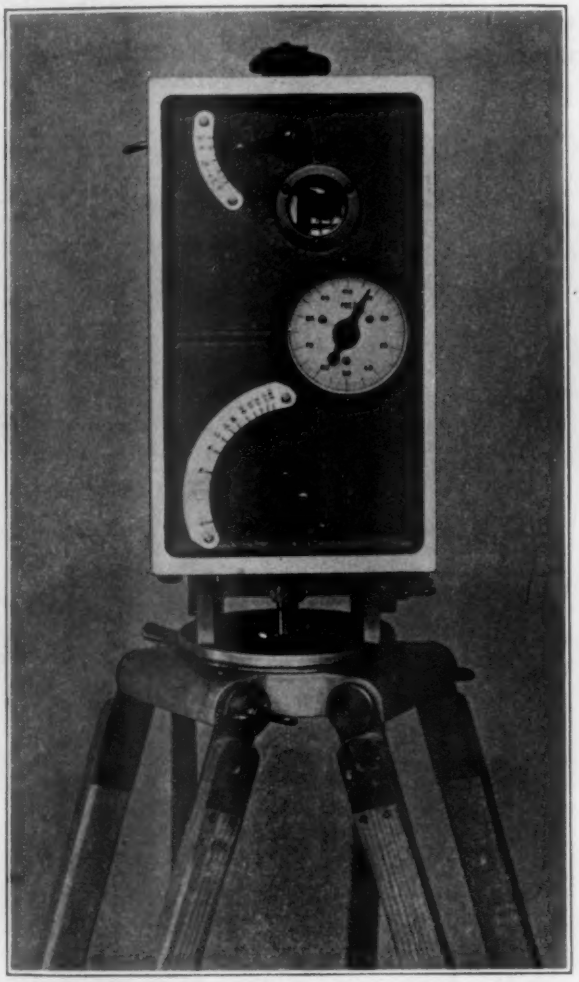
Front of the Cine Kodak.

very great. The cost of making a negative and projecting the picture upon the screen is approximately fifteen cents for each foot of film, which in projection lasts one second on the screen.

Motion pictures are obtained by making a series of photographs of the object upon a long strip of film, each picture being a representation of the object at one particular moment. Sixteen of these pictures are taken every second, and when they are

projected upon the screen, the different phases of movement blend together and give the appearance of motion. The film is held

FIG. 2.

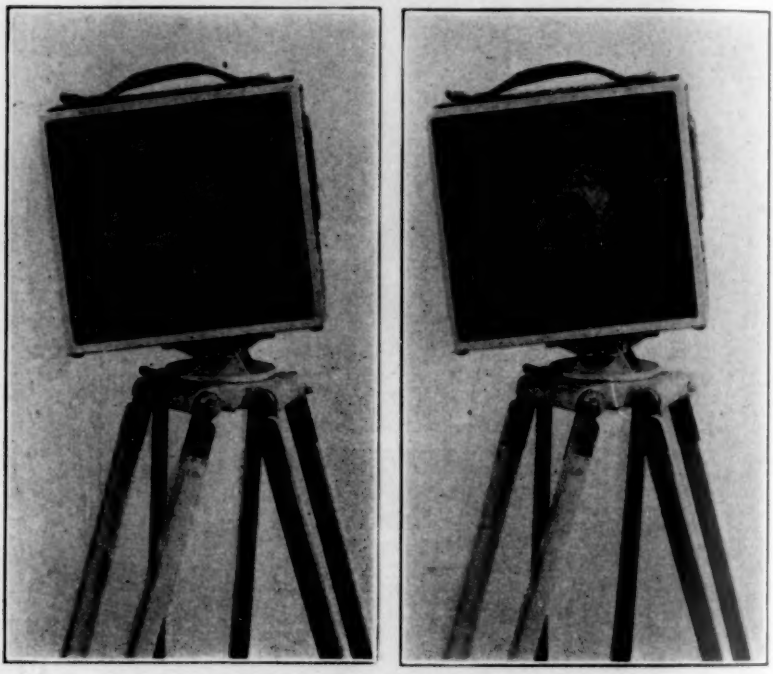


Back of the Cine Kodak.

stationary while the picture is taken or projected and then is moved forward very quickly to a new position and is held still again, so that sixteen times a second the film is moved forward,

and sixteen times a second it must be stopped. This movement is accomplished by what is called the " intermittent " mechanism in the camera or projector, the film being pulled down by claws which catch in the perforations, pull it down into its new position by the height of one picture, and then come out of the perforations again, leaving the film motionless until, as the movement

FIG. 3.



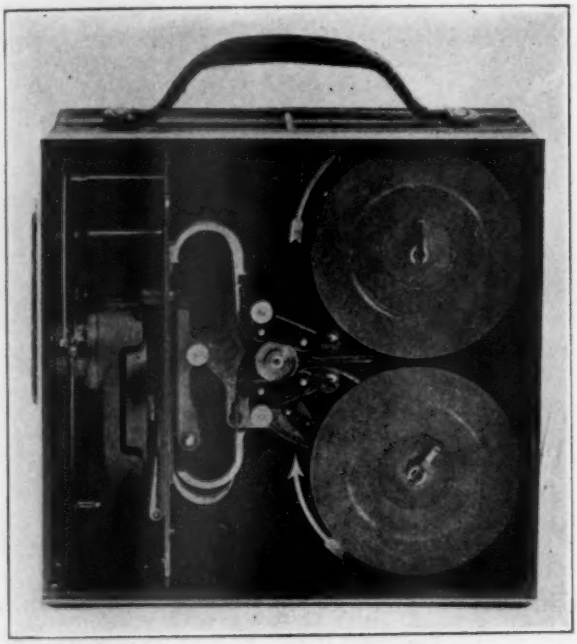
Crank side of the Cine Kodak.

of the mechanism continues, they re-engage and pull the film down again. In projectors, a sprocket with teeth on it instead of claws, which engage in the perforations, is sometimes moved intermittently to pull the film down.

The whole system of amateur motion picture photography which has been worked out by the Eastman Kodak Company is founded on film smaller than that used in the standard camera and on a new process used in finishing it, but of almost equal importance is the design of the apparatus in which the film is used.

The camera was designed and built in the instrument shop of our optical factory and is, on the whole, of standard type. It resembles, in fact, a standard motion picture camera of the highest grade, but in amateur size. No attempt has been made to cheapen the camera by the omission of any necessary feature or by any undue simplification. Our object was to produce an instru-

FIG. 4.



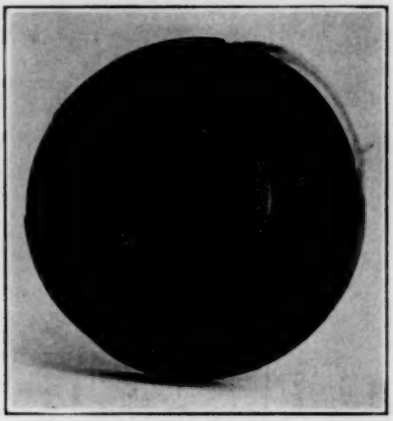
Mechanism with the door removed—with film.

ment which would take pictures equal in every respect to those which the professional could obtain. The lens is a kodak anastigmat working at f/3.5, which enables photographs to be taken under the worst conditions of light. The finder is just above the lens (Fig. 1) and by an ingenious attachment changes the position of its image as the lens is focused, thus always showing the image in the correct position. The lens has a focusing lever carried through to the back which can be focused for any distance from infinity to four feet. The diaphragm control is in the left-

hand corner and can thus be read easily. In the centre of the back is the footage indicator which shows the number of feet of film which have been used (Fig. 2). The crank is put out of the way into a recess when not required (Fig. 3). It is turned normally twice a second, taking pictures at the standard rate of sixteen pictures a second. The mechanism is of the standard motion picture type (Fig. 4), the film being pulled down by means of a claw operated by a cam mechanism.

In order to load the camera, the film spool (Fig. 5) has its outer cover removed and is then placed on the upper spindle pro-

FIG. 5.

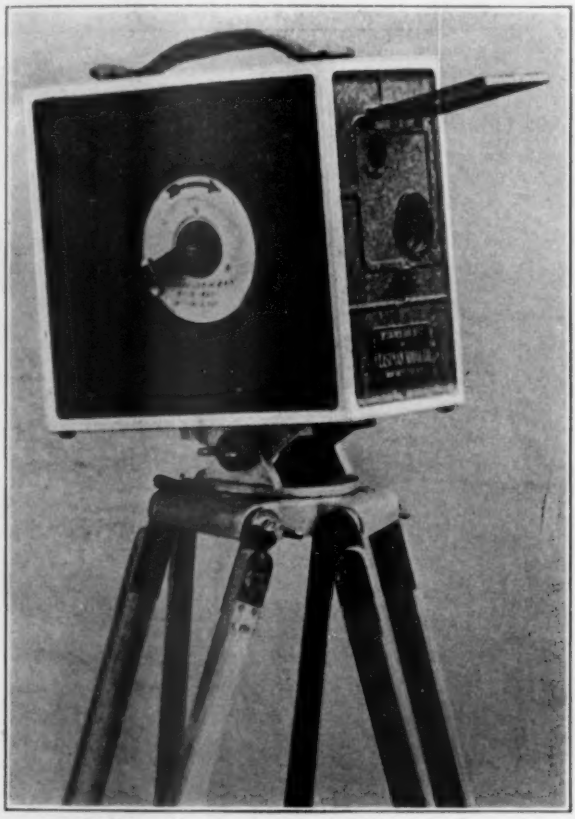


Film spool.

vided for it. To the film there is attached a paper leader of the same width as the film and perforated in the same way. Two feet of this are pulled out and are threaded over the sprocket of the camera on to which it is held by a presser plate, down through the gate, where the claws engage in the perforation, a loop being formed above the gate, as is indicated on the camera mechanism, through another loop, which is also indicated, back under the sprocket, and thence to the bottom spool, in which the end of the paper is inserted, and a few turns made to ensure everything being right. The inner cover is then removed from the spool, the film being protected for a few seconds only by the paper leader. The door is placed on the camera, and the four remaining feet of paper leader are run off. The footage indicator

at the back of the camera is then set at zero, and the camera is loaded ready for use with 100 feet of film. After all the film has been exposed, cranking is continued for five more feet, thus winding up another paper leader on to the exposed film. The

FIG. 6.



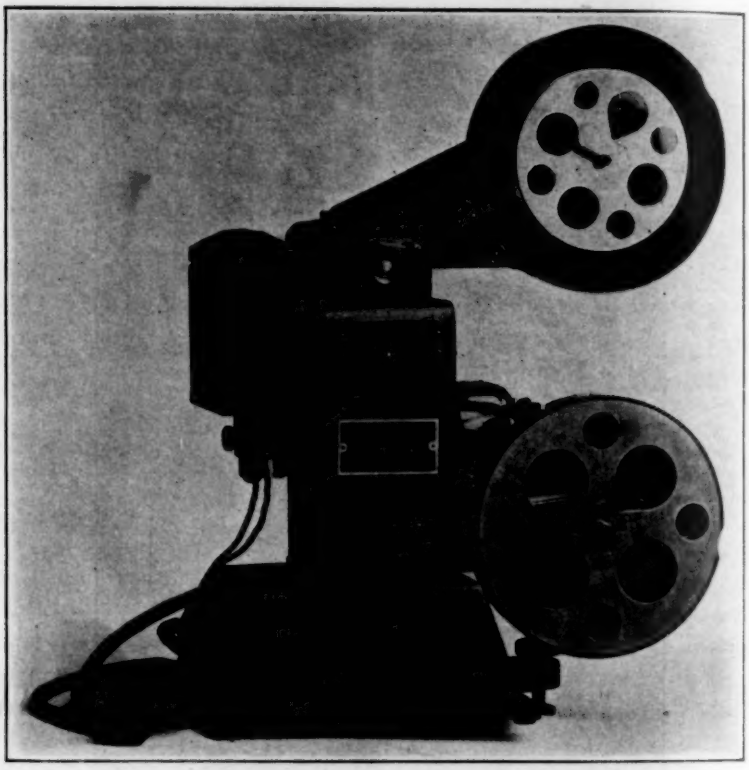
Cine Kodak on its tripod.

camera door can then be opened, the covers put on the spool of exposed film, and the spool removed and sent to the Kodak Company for development.

It is proposed to supply the camera either for use with the hand crank or with an electric motor attachment by which it can be cranked by the aid of a storage battery of very small size

carried by the user. When cranked by hand, the camera is used on a special tripod made to be as light and yet as rigid as possible, the tripod head being made to rotate and to move in a vertical direction for the convenience of the operator (Fig 6). It is not intended that the tripod head should be used to produce panoramic

FIG. 7.



Kodascope projector.

pictures by rotating while the camera is being cranked. It is extremely difficult to do this smoothly, and the result when obtained rarely gives a pleasing impression when projected. A rotating head is necessary to enable the camera to be moved in direction rapidly in order to follow objects in the field. When the camera is used with the electric motor, it is not necessary to use a tripod, though it is convenient to rest the camera upon

something, and for this purpose a simple walking stick has been devised with a screw which fits into the tripod stick of the camera.

FIG. 8.

Kodascope with lamp house open.

This makes it possible to rest the camera and hold it steadily by the hand. The weight of the camera loaded is eight pounds; with the motor, ten and one-half pounds. The weight of the storage battery is two and one-half pounds, and of the tripod with

its special head, nine pounds. The camera on the tripod thus weighs seventeen pounds and the motor-driven camera with the storage battery, thirteen pounds. After the film has been developed, the positive is ready for projection.

The projector, which is called by us the "Kodascope," is, like the camera, a standard projector of the highest grade with such changes as are necessary to make it suitable for use by amateurs and for the small film (Fig. 7). The mechanism is of the same claw and cam type as the camera. The film, which is usually assembled in 400-foot reels, which are equivalent to 1000-foot standard reels and last for sixteen minutes on the screen, is placed on the upper shaft and the film is threaded on to an upper sprocket which feeds the film in a loop to the gate (Fig. 8), then through the lower sprocket to the take-up reel, which is placed on the bottom shaft. The Kodascope is driven by a motor, and the light is supplied by a mazda lamp through a condenser which is attached just behind the gate. The lens is of very high aperture, specially designed and built by us, and has a focusing mechanism of a convenient type. This high aperture lens and efficient condenser system give a bright image on a screen with a small lamp, and for home use the apparatus is arranged to give a satisfactorily bright screen of 4½ feet in width, the two standard sizes of screens for home or classroom use being 30″ × 40″, which is large enough for the ordinary room, and 40″ × 54″, which is preferable for very large rooms or classrooms. By changing the lamp house and attaching a more powerful lamp with a special condenser system, a school can use a seven-foot screen and obtain ample light on it.

The Kodascope is entirely automatic in its operation. Once a film is threaded, there is no need to go near the machine until the film is exhausted, so that the operator is quite unnecessary, and the user can sit at ease among his friends while his pictures are being shown. The machine uses a lens of two-inch focal length and fills the 30″ × 40″ screen at eighteen feet distance and the 40″ × 54″ screen at twenty-four feet distance. The weight of the Kodascope projector with its motor ready for use is twenty-three pounds.

The quality of the picture depends upon three points: The optical perfection of the systems used in the camera and projector, on which depends the sharpness of the pictures that are taken;

the mechanical perfection, on which depends the steadiness of the pictures on the screen; and the photographic quality of the emulsion and the process used, on which depends the faithfulness with which the brightnesses in the light intensities in the original pictures are reproduced and the consequent fidelity to nature and also the appearance on the screen as regards any structure or graininess.

Now, when a small film is used for amateur photography, the

FIG. 9.

On left, small image marked *A*; on right, enlargement of small image to 55 diameters showing graininess.

accuracy required on all these accounts is increased, although fortunately the strains both on the film and on the mechanism are decreased. The lenses must be of the highest quality, since the small pictures will be enlarged to a greater degree than big pictures and must consequently be sharper. The mechanical accuracy must be higher, since any failure in perfection of register will be perceptible. The photographic quality must be at least as good if the user is to be satisfied with the result he is to get.

A number of inventors have designed cameras and projectors for amateur use in which the pictures were much smaller than those used on the standard film. The chief difficulty which is introduced when small pictures are used is the graininess which such a small picture shows when it is enlarged upon the screen.

A photographic image of any kind is composed of small clumps of the microscopic silver grains, and when it is very much enlarged these clumps show and give a structure to the image. In Fig. 9 we see at the left, at *A*, a very small image, and on the right the same image enlarged fifty-five diameters. It will be seen that the detail of the image is entirely lost owing to the graininess shown. The graininess in ordinary motion pictures is very slight but is visible when the observer stands close to the screen, and it is clear that if much smaller pictures are to be used and enlarged to the same size on the screen, the results would be greatly inferior to those obtained by the use of standard apparatus and that unless something can be done to diminish the graininess, the results would not be satisfactory in comparison with the pictures shown at the theatres. Moreover, even when a smaller film is used the cost, although diminished, is still high; a negative must be developed and a positive printed from it. This printing requires very skilled work. It is rare in standard motion picture practice for the first print from a negative to be entirely satisfactory, and to get a single print of high quality from every negative would be very difficult. The use of a small film treated like the regular film would, therefore, present two difficulties—high cost or low quality of results and the graininess of the image

The ideal process for amateur use would clearly be one in which the original picture was available for projection on to the screen. In still photography it is an advantage to make negatives, because usually a number of prints are required from a single picture, but in motion picture work in most cases an amateur is interested in getting only a single print, and there are great advantages in a process which enabled a positive to be obtained by the direct treatment of the original exposure. The preparation of positives direct is well known in photography. The usual method is to develop the exposed image and then to dissolve out the silver in a "bleaching" bath, as it is called, which oxidizes the silver and leaves the undeveloped silver bromide intact. After exposure to light, this remaining silver bromide is developed in its turn and this gives a positive. This process has two disadvantages: It can give satisfactory results only through a very small range of original exposures because, if the exposure is too low, the amount of silver halide undeveloped is correspondingly large, and the final image is dense, while if the first exposure is heavy, there is not

enough silver salt left to form a satisfactory image. It is also dependent upon very exact evenness of coating. If the coating is too thick, then the whole positive will be overlaid by a deposit of silver which the first exposure could not reach, and if it is too thin, there will not be sufficient silver to give density in the final image. Variations in the evenness of coating will show very badly in the finished picture. As the result of a great deal of research work, a process was devised in our research laboratory which overcame these disadvantages. This process is the subject of an application for a patent, and its exact nature cannot there-

FIG. 10.

Enlargement from standard film and Kodascope positive to same magnification to show relative graininess.

fore be revealed at the present time. But it is possible now to obtain first-class positives upon coatings of any thickness whatever, the density not being dependent upon the evenness of the coating, and the control over variations of exposure quite as good as is possible if a negative be developed, and a positive be printed from it in the ordinary way. Moreover, these reversed pictures were found to be astonishingly free from graininess. The graininess is due to the large clumps of silver halide grains present in the emulsion. These large clumps are more sensitive to light than small or widely separated grains, and therefore when a short exposure is made, the large clumps are the first to become exposed. These are removed in the reversal process, and the final image is

made up of the grains of the least sensitiveness. Since these are the smallest grains and the smallest clumps of grains, such a direct positive image shows very little graininess. In Fig. 10 there is shown at the left, an enlargement from a standard motion picture print, and on the right the same scene taken on the small film and enlarged until it is the same size as the picture taken on the standard film. It will be seen that the small film is so free from graininess that a picture of the same size shows very little more graniness than if it had been made by the standard process.

The development of the film is quite a complicated process and requires very special and complicated equipment since the film has to go through a great number of treatments compared with the simple operation of developing and fixing to which motion picture film is usually exposed, and for this reason it has been decided that for the present, at any rate, the Kodak Company should undertake this work itself, and it is installing equipment which will make it possible to finish all the film that can be taken with the cameras in use.

Naturally, many amateurs will wish to have more than one print for some special reason, and this is provided for by the use of a special printer in which a positive can be duplicated, the duplicate being reversed into a positive in the same way as the original picture. In this way, it is possible to obtain duplicates at the same cost as the original picture, and though this is somewhat higher than the cost of making prints from an ordinary negative, there is no question that the use of the reversal process will greatly cheapen the production of motion pictures by amateurs. The small pictures can be enlarged in special printers to make pictures of the standard size required for theatres. This will no doubt not be required very often, but what will be done to a very large extent is that the pictures of standard size will be reduced to make the small prints suitable for projection in the Kodascope.

Fig. 11 shows Kodascope film side by side with the standard film. The Kodascope film was standardized as being 16 mm. wide compared with the standard width of 35 mm. The picture is 1 cm. × ¾ cm. or 10 mm. × 7½ mm. compared with the standard picture of 1 inch × ¾ inch, so that the area of the picture is approximately one-sixth of that of the standard picture. The film has only one perforation on each side per picture, while the

standard has four perforations. This has the advantage that it is impossible to misframe the picture. If it is framed at all, it must be framed right on the screen. It will be seen that five pictures on this small film occupy the same length as two pictures on the standard film. The small film, therefore, has forty pictures to a foot whereas the standard film has only sixteen pictures per foot, and while a foot of standard film lasts only a second on the

FIG. 11.

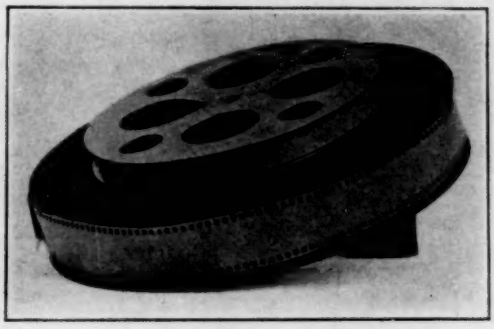
Kodascope film side by side with standard film.

screen, a foot of the Kodascope film lasts two and a half seconds. The spool used in the Cine Kodak takes 100 feet of the small film, corresponding to 250 feet of the standard film, and the Kodascope projector reel takes 400 feet, corresponding to the standard thousand-foot projection reel, which runs for sixteen minutes (Fig. 12). The small size of the Kodascope film naturally makes its cost much less than that of standard film. It costs approximately fifteen cents to take a negative, develop it, and make

one print on standard film for each second on the screen; that is, for each foot of film, so that to make a standard film of 1000 feet will cost $150. The Kodascope film will cost about two and a half cents a second, so that a reel running for one thousand seconds will cost $24. The cost of the film which is rented will, of course, be correspondingly lower in the smaller sized film, so that an evening's entertainment at home will be obtainable for a very reasonable sum.

In order to get some idea of what this means to the amateur, it is necessary to remember how long a picture should be. Experience has shown that a view of a stationary object, or one in which

FIG. 12.



Standard reel and Kodascope 400-foot reel.

the movement is repeated, such as a water fall or a game, and in which there is no continuity in the action, should last on the screen for between 5 and 10 seconds. This may seem short, but trial shows that if a scene of this type lasts for more than 10 seconds the audience wearies of it. When taking pictures with the Cine Kodak, therefore, it is desirable to give about 7 or 8 seconds' exposures to each scene, moving the camera from one point to another in order to get variety. The cost, therefore, of a single scene taken with a Cine Kodak is about twenty cents, and this compares favorably with the cost of taking an ordinary kodak picture, developing the negative, and making one print. On the whole, it appears as if amateur cinematography with the Cine Kodak will not be more expensive to the user than is still photography.

The film base used for making the Kodascope film is the slow-burning film made from cellulose acetate. While the cellulose nitrate film commonly used in motion pictures is entirely safe for theatrical work where proper precautions are taken to prevent

FIG. 13.

Enlargement of single small picture.

any risk of film fires and to quench a fire should it arise, the introduction of such film into the home or school is most dangerous, and one of the great advantages of using a special size of film is that it will not be possible to obtain this film in the fast-burning nitrocellulose stock. For the same reason, though to a lesser degree, it is an advantage that this new film cannot be cut from

film of standard size by any simple operation. Several small projectors that have been built recently have been made to take half-width film, to be obtained by slitting standard perforated motion picture film in half. While, of course, it is intended that slow-burning stock only should be used for this purpose, there is always the danger that some one would be tempted to use the cheaper nitrate stock and to slit it in half for use in the narrow width. The same objection applies with much greater force to the use of projection machines taking film of standard width. It is probable that in the near future there will be a number of projectors on the market and possibly some cameras also taking the 16-mm. film, so that the 16-mm. size may become a standard throughout the entire trade for small film used for amateur cinematography just as the professional 1⅜-inch film, used first by Lumière and Edison, became the standard for all motion picture work.

The single small pictures taken on the Cine Kodak can be enlarged, and so fine is the grain and so good the definition that the results of enlargements of these extremely small pictures, which, if examined in the hand, need a microscope to see the detail, are of surprising quality. One of these enlargements is shown in Fig. 13.

The first equipment to be put on the market by the Kodak Company will be in the form of an entire outfit for taking and projecting the pictures. It will include the camera with its tripod and tripod head, the Kodascope with the screen, and the necessary accessories, such as a device for joining the films together. The price has not been definitely settled yet, but it will be in the neighborhood of $300, and with the outfit an amateur will be equipped to take his own pictures and project them or those taken by other people.

The introduction of motion pictures into the home will, of course, produce a demand for pictures other than those taken by the owner of the machine, and we are arranging therefore to supply for the Kodascope a library of films made by the reduction of standard reels to Kodascope size. We hope in the next year to have several hundred subjects available, including scenic pictures, stories for children, and pictures of all kinds of a type suitable for use in the home. We believe that the spreading use of the motion picture at home will increase the public interest in

the motion picture and will rouse the interest of many people who have not, up to the present, been regular attendants at the motion picture theatres, so that they will follow the progress of the art and will take a real interest in the development of pictures as shown in the large theatres. Just as the widespread use of photography by the amateur has been the chief contributing cause to its marvelous development in the last thirty years and to its extension to every field of human activity, so I believe the use of the motion picture by photographers throughout the world will make possible developments in the art of motion picture that are at present undreamt of, and that the use of the motion picture in schools, institutions, and homes has a future to which the Cine Kodak and Kodascope will contribute in no small degree.

Wilhelm Hallwachs. OTTO WIENER. (*Physikal. Zeit.*, Nov. 15, 1922.)—On the 20th of June, 1922, this distinguished German physicist died. His name is inseparably linked with the effect that he discovered. Shortly after Hertz had performed his epoch-making investigations, proving the existence of electrical waves from which wireless telegraphy and telephony have sprung, Hallwachs found that ultra-violet light falling on a zinc plate negatively charged causes it to lose its charge. If the plate were positively charged it was not so discharged. Paper after paper brought to light the phases of this effect, but there came a pause of fourteen years in his investigations on this subject. About 1904 he resumed his photoelectrical activity and succeeded in solving many questions in this field. "Question follows question and step by step each is answered with thoroughness by means of experimental skill." This investigation is only the best known of his contributions to physics.

He was the son-in-law of Friederich Kohlrausch, whose assistant he was at Strasbourg. There are American students who will recall with pleasure their acquaintance with this genial and gifted experimenter. G. F. S.

Discharge of Electrons from Electrodes Nearly in Contact. FRANZ ROTHER. (*Physikal. Zeit.*, Oct. 15, 1922.)—In 1911 this Leipzig physicist showed that a current flows from one electrode to another even with small differences of potential, provided the distance separating the two is exceedingly small. When the interval is as short as a light wave, 10 volts cause a current of 10^{-14} ampere to flow across. The experiments leading to this result were conducted in air at pressures of 760 and of .5 mm., and pressure appeared not to influence the result. To test this conclusion it was desired to repeat

the investigation, using the highest attainable vacuum. The problem was then to devise a way of mounting two electrodes in such a vacuum so that their distance apart could be varied and, more than that, measured with great accuracy. Two methods of moving the electrodes were available, electrostriction and the bending of a metallic membrane. One electrode was attached to an iron rod whose length was varied by changing its magnetization. This plan was defective when it was needed to bring the electrodes into actual contact. In the second method the electrode was carried by a platinum membrane whose form was governed by the difference between the pressure in the tube and the external pressure. This met the requirements more completely than the former method. The measurements of distance were made by an interference arrangement. The electrodes were metal cylinders 4 mm. in diameter with polished hemispherical ends.

For platinum hemispheres of radius 20 mm. in a high vacuum, a current of about 5×10^{-14} amperes flowed from one electrode to the other, 250 millionths of a millimetre distant, when the difference of potential was 190 volts. The increase of current with voltage was rapid. Electrons appear to be driven out of the metal by a sort of "cold Richardson effect." G. F. S.

The Thermal Effect of Vapors on Rubber. A. S. HOUGHTON. (*Proc. Phys. Soc.*, Dec. 15, 1922.)—Into carbon dioxide were plunged two exactly similar thermometers, the bulb of one of which had been covered with a thin film of rubber, left by the evaporation of a rubber solution. The latter instrument showed a higher temperature.

Lengths of copper and Eureka wire were soldered together, the kinds alternating. The first, third, fifth, etc., junctions were exposed to vapors while the even junctions were protected from them. Immediately on exposure a galvanometer joined to the series of wires indicated a sudden rise of temperature. This became zero as the exposure continued. Upon the withdrawal of the junctions there appeared a sudden cooling which in turn disappeared after a time. The vapors of chloroform, benzene, toluene, pyridine and oils of lavender and guaniol showed the effect. Ammonia and carbon dioxide are known to pass through rubber. These gases showed the effect, but the heat developed was not great. Moist air gave the effect very clearly.

The greatest difference of temperature produced by the presence of the rubber was about one degree.

The heating of cellulose by water-vapor seems akin to the effect above described. "Rubber differs, however, from cellulose in its non-fibrous structure and wide range of action with vapors. So it is probable that only a part of the heat produced is due to the condensation of the vapor on the rubber, and the additional heat is supplied either by some form of chemical union, or by the formation of a solid solution between the vapor and the rubber." G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

INVAR AND RELATED NICKEL STEELS.[1]

[ABSTRACT.]

THIS circular is mainly a compilation of data obtained during the last thirty years by various investigators on the different properties of nickel steels. Particular attention is given to "invar," a nickel-iron alloy containing about 36 per cent. nickel and possessing an extremely small thermal expansivity at ordinary temperatures, the mean coefficient of linear expansion between 0 and 40° C. being on the order of 1 to 2 millionths. The results of investigations made on the various properties of the nickel-iron alloy series have been presented largely in diagrammatic and tabular form.

Following an historical account of the development of nickel steels and studies of their properties, the nature of the anomalies in behavior met with in these steels and characterized by their irreversible and reversible phenomena are discussed in the light of the results obtained on their various physical properties. The constitution and microstructure of these alloys are first dealt with, and next the rather extensive studies made on the magnetic properties. A magnetic transformation (Curie points) diagram has been plotted from the observations obtained magnetically, for the most part, by various investigators.

Anomalies in the change of electrical resistance with temperature are shown to be present in nickel-iron alloys. It is seen from the diagram for electrical resistivity at ordinary temperatures, plotted from data obtained on pure ferro-nickels, that there is a sharp increase in resistance for those alloys containing about 30 to 35 per cent. nickel—the resistivity of invar being on the order of 80 microhms-cm.

The anomalous behavior in the thermal expansion of nickel-iron alloys at various temperatures is illustrated by a number of diagrams, and the rule of corresponding states formulated by Guillaume has been applied in interpreting some of the results. The degree of thermal expansivity reaches a minimum in alloys

* Communicated by the Director.

[1] Circular No. 58, second edition, price thirty cents.

with about 36 per cent. nickel (and 0.4 per cent. manganese and 0.1 per cent. carbon), and the position of this minimum may be modified by the presence of added elements as chromium, etc., and also by thermal or mechanical treatment. The theories advanced as an explanation for the anomalous behavior in the expansibility of nickel steels are briefly dealt with. In addition to the principal characteristics of thermal expansion, there are certain secondary phenomena of a transitory and of a progressive nature occurring over small ranges of temperature or even at constant temperatures over a long period of time which affect the constancy in the dimensions of the invar. An aging process or special heat-treatment is employed to reduce these secular changes to a minimum. The cause of this instability of nickel steels has been found to be due to the presence of carbon.

The thermal conductivity and specific heat of nickel-iron alloys show minimum and maximum values, respectively, at about 35 per cent. nickel.

Some data on the mechanical properties and also Brinell and Shore Scleroscope hardness of nickel steels, with the nickel content ranging up to about 50 per cent., are given in tabular and in diagrammatic form. The tensile properties of invar may run as follows: Tensile strength, 50,000–100,000 pounds per square inch; elastic limit, 30,000–70,000 pounds per square inch; elongation, 25 to 50 per cent.; and reduction of area, 40 to 70 per cent.

Nickel steels present anomalies in the elastic modulus, corresponding closely to those found in thermal expansion. It has been found that the degree of anomaly can be reduced in very large measure by means of suitable additions made to the alloy, namely, about 12 per cent. chromium or its equivalent, this alloy having recently been introduced under the trade-mark "Elinvar." This is of practical importance in the construction of watches and chronometers, where the degree of error with variations of temperature and consequent need for compensation may be made very small.

Resistance to corrosion by fresh and sea water and acid liquors increases with the proportion of nickel. An alloy containing about 18 per cent. may be regarded as practically non-corrodible. The resistance of invar to oxidation, while very much greater than that of ordinary steel, is not perfect, therefore it is advisable to

coat an invar instrument with a protective coating as vaseline, if it is to be exposed for a long time in a moist atmosphere.

The extent and nature of applications of nickel steels are discussed. A list of makers of nickel steels and dealers in nickel steels of minimum thermal expansivity in America and also a selected bibliography are included.

RECOMMENDED SPECIFICATION FOR QUICKLIME FOR USE IN CAUSTICIZING.[2]

[ABSTRACT.]

THE manufacture of caustic alkali consumes a large tonnage of quicklime annually. For this purpose a very pure grade of lime is required. Purity is determined not by the total content of calcium oxide, but rather by the content of calcium oxide which is available in the process for which the lime is used. A careful study of the requirements of the users of the quality of lime which is actually being used and of the possibilities of production have led to the establishment of 85 per cent. as a fair standard for available lime. Unlike most materials which are bought on specification, chemical lime is more valuable if it has a higher degree of purity than that required by the standard and less valuable if it has a lower degree. For this reason we have recommended that a bonus and penalty clause be inserted in the contract in order to take care of variations from the 85 per cent. While the material is less valuable, but can still be used if the purity falls below the standard, there is a point reached eventually when the value of the material becomes such that it is poor economy to use the lime for this purpose. A careful survey of the situation has led us to set this figure at 70 per cent. In working up the details of this specification the bureau has been assisted by an Interdepartmental Conference on Chemical Lime, composed of representatives of various government agencies. The specifications have been partially approved by the National Lime Association, representing the producers, and by the Technical Association of the Pulp and Paper Industry, representing the largest group of consumers of this kind of lime.

[2] Circular No. 143, price five cents.

RECOMMENDED SPECIFICATION FOR LIMESTONE AND QUICKLIME FOR USE IN THE MANUFACTURE OF SULPHITE PULP.[1]

[ABSTRACT.]

IN the manufacture of sulphite pulp the wood is cooked with a solution of calcium bisulphite. This solution may be prepared in two ways, either by permitting sulphur dioxide to pass upward through a tower filled with limestone and allowing water to trickle down over the stone, or by passing the sulphur dioxide through milk of lime contained in a tank. In the former process high-calcium limestone is preferred, because limestone containing much magnesium carbonate is not dissolved uniformly and is thus apt to fall to pieces and stop the circulation. In the latter process a high-calcium quicklime is preferred for the manufacture of the milk of lime, because the magnesia is more soluble than the lime in the sulphur dioxide solution and a liquor having higher strength can thus be prepared. It is quite possible, however, to use a high-magnesium stone in the tower process or a high-calcium lime in the milk-of-lime process. The specifications, therefore, cover both high-calcium and high-magnesium limestone and quicklime on the basis of about 95 per cent. purity.

The Fluorescence and Coloration of Glass Produced by Beta Rays. J. R. CLARKE. (*Phil. Mag.*, April, 1923.)—Three specimens of soda glass tubing were kept in radium emanation until they had acquired a rich brown color and had ceased to fluoresce. Each specimen was divided into four parts. When a part was put into an oven it began to fluoresce and continued to do so until the brown color had disappeared. The hotter the oven the shorter the time needed to remove the color and also the more intense the fluorescent light. One specimen lost its color in the following number of minutes at the temperatures designated, 110°, 13 min.; 180°, 3 min.; 235°, 1.5 min.; 350°, .75 min. In one case at a temperature of only 95° the fluorescence lasted fifteen hours. "The decoloration of the glasses, therefore, appears to be connected with a change in the state of molecular aggregation, coloration being the reverse process. As both coloration and decoloration were accompanied by fluorescence, it is probable that the fluorescence is due to this change."

Of nineteen kinds of glass examined, fourteen turned brown and the rest purple. All that turned purple had manganese in them. The others contained none of this element. G. F. S.

[1] Circular No. 144, price five cents.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

AN ADAPTATION OF THE THALOFIDE CELL TO THE MEASUREMENT OF PHOTOGRAPHIC DENSITIES.[1]

By A. L. Schoen.

In photographic research, it is frequently necessary to measure low densities with great accuracy. The usual visual methods for measuring density have been found inadequate for this purpose. Tests made with thalofide cells to determine the conditions for high sensitivity and stability show that this instrument can be adapted as a physical photometer for the measurement of these densities.

Changes in sensitivity with applied voltage and intensity of illumination were observed. From these data the best voltage and illumination were determined and maintained constant on the cell. Densities were determined (using the inverse square law) by moving the source of illumination to produce zero deflection in a sensitive galvanometer for each step of the sensitometric strip.

Results obtained thus far indicate that this method can be used with advantage in problems involving the measurement of very low densities and small density differences and that densities as low as .005 (±99 per cent. transmission) can be measured with a fair degree of certainty.

SIZE-FREQUENCY DISTRIBUTION OF GRAINS OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS. V.—SYSTEMATIC CORRELATION.[2]

By E. P. Wightman, S. E. Sheppard, and A. P. H. Trivelli.

A series of photographic emulsions has been prepared of which a correlation between the grain and sensitometric characteristics shows an apparently close relationship. These emulsions are strictly comparable because practically all the factors in their preparation were under control, only one being varied so as to progres-

* Communicated by the Director.

[1] Communication No. 171 from the Research Laboratory of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, June, 1923, p. 483.

[2] Communication No. 172 from the Research Laboratory of the Eastman Kodak Company and published in *J. Phys. Chem.*, May, 1923, p. 466.

sively increase the speed of the emulsions in the series, and because equal weights of emulsion containing in every case the same amount of silver halide by weight were coated on the plates. The equations which represent the grain-size-distribution of these emulsions show a steady transition from a steep exponential, $y = y_0 e^{-kx}$, to a flat, widely spread Gaussian type, $y = y_0 e^{-k(x-\alpha)^2}$. That is to say, in passing through the series from the slow to the comparatively fast emulsion the parameters y_0 and k steadily decrease, while the parameter α, which is zero in the first two examples, then steadily increases.

THE RESISTIVITY OF VARIOUS MATERIALS TOWARDS PHOTOGRAPHIC SOLUTIONS.[3]

By J. I. Crabtree and Glenn E. Matthews.

OF the metals and alloys, lead, nickel, Niaco, and monel are the most resistive to photographic solutions, but are suitable only for developing and washing apparatus. Toning baths attack all metals. With fixing baths a protective layer of silver plates on the metal tends to retard corrosion. Monel is quite satisfactory for clips, hangers, and small tanks which are not permanently in contact with the solutions. Salts of copper or stannous tin cause bad developer fog, so that copper or tin alloys containing these metals, such as solder or brass, should not be used in contact with developers. Metallic contact of two different metals or alloys causes electrolysis which hastens the rate of corrosion. Lead-lined tanks are satisfactory for developers and fixing baths if the joints are lead burned. Lead piping is suitable if the joints are wiped.

Of the non-metallic materials, glass, enamelled steel, well-glazed earthenware, hard rubber and wood resist all photographic solutions. Porous earthenware, rubber composition, and impregnated products disintegrate as a result of crystallization of hypo or other salts in the pores of the material. Small dishes should be made of glass, enamelled steel or hard rubber. Deep tanks for motion picture work may be of wood (cypress), lead-lined wood, Alberene stone or slate, well-glazed stoneware, or Portland cement. Piping should be of lead, hard rubber, or glass.

[3] Communication No. 176 from the Research Laboratory of the Eastman Kodak Company and published in *Ind. Eng. Chem.*, July, 1923, p. 666; *Brit. J Phot.*, June 15, 1923, p. 366.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

COMPOSITION OF FREE FATTY ACIDS OF COTTONSEED OIL.[1]

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE fatty acids of cottonseed oil and of peanut oil are set free by hydrolysis in practically the proportions in which they occur as glycerides in the oils. The same probably is true of the fatty acids in all other vegetable oils.

GROUNDING COTTON GINS TO PREVENT FIRES.[2]

By Harry E. Roethe.

[ABSTRACT.]

THE installation of grounding systems for removing electrostatic charges in cotton gins is one of the most effective means of preventing fires in gins. The U. S. Department of Agriculture has developed an inexpensive and effective grounding system. Many insurance companies in the South give lower insurance rates for gins having a proper grounding system.

CHEMICAL, PHYSICAL, AND INSECTICIDAL PROPERTIES OF ARSENICALS.[3]

By F. C. Cook and N. E. McIndoo.

[ABSTRACT.]

THE Bureau of Chemistry has determined the chemical and physical properties of a large number of commercial arsenicals and a large number of arsenicals prepared in the laboratory. It has also determined the compatibility of various mixtures of arsenicals with other insecticides and fungicides. The Bureau of Entomology has determined the comparative toxicity of the same arsenicals.

* Communicated by the Chief of the Bureau.

[1] Published in *Cotton Oil Press*, 7 (June, 1923) : 35.

[2] Issued as *U. S. Dept. Agr. Cir. 271* (May, 1923).

[3] Issued as *U. S. Dept. Agr. Bul. 1147* (June 8, 1923).

From this work the conclusion is drawn that a chemical analysis of an arsenical does not give sufficient data to judge satisfactorily its insecticidal properties and a toxicity study alone does not show that an arsenical is suitable for general insecticidal purposes. Both a chemical analysis and a toxicity study are necessary to show whether or not an arsenical is a satisfactory insecticide.

EFFECTS OF TREATING MATERIALS AND OUTDOOR EXPOSURE UPON WATER RESISTANCE AND TENSILE STRENGTH OF COTTON DUCK.[1]

By T. D. Jarrell and H. P. Holman.

[ABSTRACT.]

WATERPROOFING materials frequently hasten deterioration in the strength of canvas exposed to the weather. Waterproofing treatments free from mineral pigments made canvas after exposure weaker than the untreated canvas after exposure. Preparations containing an excess (over 50 per cent.) of asphalt or coal-tar pitch usually caused less deterioration in strength and gave greater water resistance than other treatments free from mineral pigments. The addition of mineral pigments to certain waterproofing preparations which have a deteriorating effect on canvas when exposed to the weather materially reduced this effect, and in some instances made the treated canvas stronger than the untreated canvas after exposure. Usually the addition of pigments did not interfere with water resistance and sometimes materially increased the water resistance.

On Tidal Stresses and Continental Displacements. H. H. POOLE. (*Phil. Mag.*, March, 1923.)—Eddington has given .001 second as a probable value of the increase in the length of a day produced by the action on the earth of tidal forces during a century. Using the moment of inertia of the earth about its axis (9.74×10^{44} gram sq. cm.) the author calculates that to produce the specified lengthening of the day, a uniform force acting over the entire surface of the earth would be adequate if it amounted to the weight of a kilogram per square kilometre. This force is too small to have produced much displacement of the continents. "It would seem then that, if tidal stresses have played a part in the history of the continents, they must have done so in past epochs, when, owing to crustal weakness or the closer proximity of the Moon, they were far more powerful than at present." G. F. S.

[1] Published in *J. Ind. Eng. Chem.*, 15 (June, 1923): 607.

NOTES FROM THE U. S. BUREAU OF MINES.*

COMPARISON OF GAS MASKS, HOSE MASKS, AND OXYGEN-BREATHING APPARATUS.

By S. H. Katz and J. J. Bourquin.

THREE types of respiratory apparatus, namely, gas masks, hose masks, and self-contained oxygen-breathing apparatus, are now commonly used for protection from noxious gases, vapors, and smokes or mists, but no particular type can be selected as best for all conditions. Many factors must be considered in connection with each situation, so that each must be considered as a problem in itself.

Gas masks are the simplest and easiest to wear, also the least cumbersome, but they protect only in comparatively low concentrations of noxious gases and should never be used where the air contains less than 16 per cent. of oxygen. Special masks give protection from one gas or class of gases, but may give no protection against another gas or class of gases.

Hose masks protect in any irrespirable atmosphere, but are somewhat cumbersome, the length of hose limiting the distance a wearer may go from fresh air. They are serviceable also where a supply of pure air moves with the wearer, as where a locomotive engineer in a smoky tunnel is using a hose mask supplied with air from the compressed air line of the locomotive. Hose masks consume no chemicals or materials and so are not limited in the time they may be used.

Self-contained oxygen-breathing apparatus protect in any irrespirable atmosphere, but their weight is cumbersome, they can be used only by trained men, and frequent attention must be given them to maintain good working condition. On the other hand, they are the only safe means for exploring mines and other places filled with irrespirable gases in high concentrations.

More complete statements concerning the properties of each apparatus are given in Serial 2489, recently published.

* Communicated by the Director.

RESULTS OF ASSAYS OF THE NEW ALBANY OIL-SHALE.

By John R. Reeves.

IN a general survey of the oil-shale resources of Indiana, other papers have already been published which present data with reference to the following points: (1) Distribution of the New Albany shale; (2) amount of shale available; (3) homogeneity and thickness of the formation; (4) amount and quality of the oil obtained from the shale; (5) nitrogen content of the shale; (6) extractibility of the shale and its amenity to breaking; (7) some economic factors bearing upon the utilization of the shale; and (8) other miscellaneous factors and data. In the future, technical work on other phases of the general problem is expected to be done with the object of making a complete survey of this resource which is of much potential importance to the State and Nation.

There was recently completed an analytical survey of samples systematically collected from the outcrops, representing complete sections of the New Albany formation at different points in the district.

Each sample was tested for oil yield, water yield, specific gravity of crude oil, distillation of crude oil (atmospheric distillation ending at 275° C.), unsaturation of tops (fraction boiling to 275° C.), carbon residue of residuum from atmospheric distillation, yield of scrubber naphtha, and percentage of nitrogen.

The oil yield varies from 4.8 gallons per ton to 15.7 gallons per ton. The average yield for all samples is 10.3 gallons per ton. The specific gravity of the crude oil varies from 0.924 to 0.955. The average of all samples is 0.943.

The unsaturation of the tops varies from 39.0 per cent. to 45.0 per cent., the average of all samples being 42.1 per cent.

The carbon residue of the residuum from the atmospheric distillation (end point 275° C.) varies from 4.95 per cent. to 7.67 per cent., the average of all samples being 6.3 per cent. The amount of scrubber naphtha, at the rate of retorting used in this work, varies from 0.31 gallon to 1.83 gallons per ton.

The total nitrogen of the New Albany shale varies from 0.107 per cent. to 0.777 per cent., the average for 15 samples being

0.381 per cent., equivalent to a theoretical yield of 35.89 pounds of ammonium sulphate per ton. Further details are given in Serial 2492, just issued.

ATMOSPHERIC CONDITIONS IN UNION PACIFIC TUNNELS.

By S. P. Kinney.

The Department of the Interior has recently investigated the atmospheric conditions in tunnels of the Union Pacific Railroad in Utah and Wyoming, by observations made from the cabs of freight locomotives. This work was conducted by the Bureau of Mines at the request of, and in coöperation with, the Union Pacific Railroad Company, and was brought about by several accidents to members of engine crews, while passing through tunnels, from pollution of the tunnel air by exhaust gases from freight locomotives.

As a result, the causes of the gassing accidents were determined, the composition of the air in locomotive cabs while passing through railroad tunnels; the effect of these conditions on the engine crew; and recommendations made for protection of the men so exposed.

Gas samples and temperature readings taken in the cabs of locomotives were used in studying the atmospheric conditions to which the locomotive crews were exposed. The symptoms and the physiological effects produced in men exposed to the atmospheres encountered were studied. The pulse rates and body temperatures were taken, and determinations of the carbon monoxide content of the blood were made. Various methods for the prevention of gassing and for the protection of men therefrom were considered and tested; among which were the use of mechanical devices for deflecting the smoke away from the engine cab, and the use of various types of gas masks and breathing apparatus.

While this investigation is a part of the safety work of the Bureau of Mines in connection with hazards from atmospheres containing carbon monoxide, the results are of particular value to railroads operating steam locomotives through tunnels, and

are also valuable to other industries where atmospheres having poisonous gases or of a high temperature and humidity may be present. Further details are given in a recent publication.

THE PYRO TANNIC ACID METHOD FOR THE QUANTITATIVE DETERMINATION OF CARBON MONOXIDE IN BLOOD AND AIR.

By R. R. Sayers, W. P. Yant, and G. W. Jones.

IT is of vital importance in all industrial and domestic accidents occurring at places where carbon monoxide might be suspected or where the symptoms are typical of carbon monoxide poisoning that a qualitative and preferably a quantitative determination be made (the extent of poisoning being of importance in deciding whether carbon monoxide was the direct or contributary cause) to show the presence or absence of carbon monoxide. This is indeed essential from a medical standpoint, as it aids in prescribing treatment and from a legal standpoint to insure justice in the claims that are often unjustly decided for want of positive evidence. Probably the best method of diagnosis is by examination of the subject's blood. Many methods for the detection of carbon monoxide in the blood have been developed, but owing to their various individual disadvantages have never come into common usage. Some of the quantitative methods are satisfactory with regard to accuracy, but require elaborate and expensive apparatus, special technic and training, or are too delicate and cumbersome for field use.

In view of the above an apparatus has been designed by the bureau, which gives accurate results in the field and laboratory, yet it is compact (can be carried in the pocket) and durable, and sufficiently simple in operation to be used without special training. By use of this method, it is possible to detect the presence of carbon monoxide in the blood in three minutes and determine the exact amount present within fifteen minutes, and on the basis of these findings, treatment administered. The method and apparatus should fulfill the needs of hospitals, industrial surgeons, safety engineers, coroners, departments of public safety, boards of health, and other allied organizations. Further details are given in Serial 2486, recently issued.

THE FRANKLIN INSTITUTE.

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NECROLOGY.

Dr. Rudolph Hering was born in Philadelphia, February 28, 1847, and died in New York City on May 30, 1923. He was educated in the schools of his native city and obtained his technical training at the Royal Polytechnic in Dresden, Germany, from which he graduated in 1867. In 1868 he became Assistant Engineer at Prospect Park, Brooklyn. In 1869–71 he served in the same capacity in Fairmount Park, Philadelphia. From 1873 to 1880 he was Assistant City Engineer in Philadelphia. He then devoted his time to private practice and was Chief Engineer of the Chicago Drainage and Water Supply Commission from 1886 to 1888, and Consulting Engineer, Department of Public Works, New York City in 1889. He acted as Consulting Engineer for water supply and sewage works in about 150 cities, including New Orleans, Los Angeles, Tacoma, San Francisco and Honolulu. He was a member of the leading civil engineering societies of the world and the author of many reports on sewerage and water supply. Doctor Hering became a member of The Franklin Institute in 1867.

Dr. Adolph W. Miller, 400 North Third Street, Philadelphia, Pennsylvania.

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BOOK REVIEWS.

PRINCIPLES OF CHEMICAL ENGINEERING. By William H. Walker, Warren K. Lewis and William H. McAdams, Professors of Chemical Engineering at the Massachusetts Institute of Technology. 8vo, vii–609 pages, 156 illustrations and one plate. New York, The McGraw-Hill Book Company, 1923. Price $5 net.

Chemical engineering and engineering chemistry are two very different topics. The latter relates to the analysis of engineering materials and has been for many years extensively treated in standard manuals. Chemical engineering, as a special branch of applied chemistry, is of comparatively recent

origin, but the enormous development of chemical industries has brought about a great expansion of the study of both practice and theory of procedures. Most handicrafts began in purely empiric methods; the study of the principles came much later. It was a characteristic of the ancient world that there was an almost complete separation of the scientist from the worker. The "philosophers," as they were called, disdained to mingle with the artisans, who were in large part slaves, or at least subject to severe masters, although in some directions, such as engraving and delicate work, the rarity of the special qualifications gave the worker a certain degree of self-assertion. Similarly to-day, the diamond-cutters constitute a powerful guild by reason of the highly specialized nature of their work.

The book in hand is not a technology. It does not discuss the procedures for the manufacture of particular substances, but treats of the principles of the standard processes that are employed in the plants in which the chemicals are made. The authors have, as stated in the preface, selected basic operations and have brought in the most modern data of physical chemistry to aid in the explanation of these procedures. The text, indeed, contrasts very strongly with that heretofore found in works on applied chemistry, mathematics being employed in giving quantitative features to the descriptions. In the presentation of these quantitative data, use is made of a unit termed the "pound mol." This is explained, together with many other important points in the first chapter on the "Elements of Industrial Stoichiometry." In this chapter the discussion of the calculation methods is very extensive. The authors regard the conversion of the metric units into the older form and *vice versa*, as essentially simple. This is encouraging to those who wish to see the bugaboo that has interfered with metric reform exorcised. The advanced character of the book is indicated by the title of the second chapter "Fluid Films." Chapters follow on flow of fluids and of heat, fuel and power, combustion, furnaces and kilns, gas producers, crushing and grinding, mechanical separation, filtration, vaporization, evaporation, humidity, humidifiers, drying and cooling; the final chapter being on distillation.

In the chapter on mechanical separation the discussion of the curious and comparatively recent flotation methods is very brief and no mention is made specifically of the oil processes. The brevity of the treatment of this branch of the subject is due to the fact that the book is an essay on the principles of the several procedures and not upon the application of them. The authors tell us that a great many flotation processes are in successful operation, but none of the many theories offered to explain the phenomena has been accepted as generally applicable. Rickard and Ralston in their work on flotation (Mining and Scientific Press, 1919) gave an interesting history of the development of the procedure, and find—as might be expected—some reference to the practice in Heroditus. An interesting and useful application of oil-separation is described in Williams' work on the diamond mines of South Africa. Oil-separation was found very serviceable in separating the rough diamonds from other minerals.

Extensive discussion is made of the processes of combustion and of the construction of furnaces and kilns. The advantages and disadvantages of

powdered and liquid fuels are presented clearly. The work is elaborately illustrated with representations of apparatus and with diagrams. The text is clearly and carefully written and presented in good form. The book is a most valuable contribution to a field which is of great and rapidly growing importance, and is another item in the evidence that the American scientist is getting out of the necessity of seeking an education abroad.

HENRY LEFFMANN.

COURS DE CHIMIE INORGANIQUE. By F. Swarts, Professor at the University of Genth. Third edition, revised and enlarged. 8vo, 714 pages, contents and index. Brussels, M. Lamertin. Fifty francs net, in paper.

COURS DE CHIMIE ORGANIQUE. By the same author. Third edition, revised and enlarged. 8vo, 652 pages, contents and index. Same publisher. Fifty francs net, in paper.

These two books present a comprehensive survey of the important data of chemistry and embody the late developments in atomic and molecular structure and the phenomena of isotopy and radioactivity. Favorable criticism can be made of the material presented, of the method of arrangement and the explicitness of the descriptions. Distinction is emphasized between physical and chemical phenomena, experiments long known and used being described for illustrations thereof. Of late years chemists and physicists have been drawing together and the two departments of science are practically now interpenetrating. There is a great deal of old-fashioned experimenting given. Under oxygen, for instance, it seems inadvisable to take up space describing the decompositions of manganese dioxide and potassium chlorate separately, and then describing the method in which they are mixed. The latter is the only one used in laboratories or at lectures when small amounts of the gas are desired, while the commercial preparation is by entirely different procedures.

Being third editions, the books do not need an extended review. They have been before the Belgian scientific public long enough to have their merits and demerits appreciated. It is gratifying to see the French text with formulas in which the exponents are inferiors, but then this is a Belgian book, and Belgian chemists are in accord it seems with their brethren in other countries except France. The mechanical execution of the book is commendable, but the most extraordinary feature is the enormous number of typographic errors. This is all the more startling when it is remembered that these volumes are a third printing and much of the matter was probably set up from type. The inorganic section contains four closely printed pages of errors and the organic section three and one-half pages. The error modulus goes further, for not only are there errors in the text which are not indicated in the errata list, but these lists contain errors. The organic list is headed "erratum," and in the inorganic list a limited checking has shown two errors. Page 2 should be page 12, and further on line 1 should be line 8. In the table of elements on page 69, the symbol for gadolinum is given as Ga and the symbol for boron is given as Bo, but this latter is evidently a deliberate change, as the same symbol is used in the section on boron and in the formula of boron compounds. It is very strange that a professor in a great university should mutilate the table of symbols in this manner. The same criticism applies to the

spelling "crypton," instead of "krypton" in this table. Curiously enough, the name is given as "krypton" in the section in which the argon group is described, although the author promptly falls from grace using the wrong spelling in the rest of the paragraph. It seems inexplicable that an intelligent chemist could be guilty of such irregularity.

Taken all in all it seems to the reviewer that notwithstanding the large amount of information in this work and attention that has been given to the modern phases of the science, the gross carelessness in the proof reading must render it an unsafe guide to the student. With a careful revision by a competent proof reader, the book would be made into an excellent manual of chemistry.

HENRY LEFFMANN.

THE FEDERAL POWER COMMISSION: ITS HISTORY, ACTIVITIES AND ORGANIZATION. By Milton Conover. 8vo, 117 pages, bibliography and index. The Johns Hopkins Press, Baltimore. $1 net.

THE WEATHER BUREAU: ITS HISTORY, ACTIVITIES AND ORGANIZATION. By Gustavus A. Weber. 8vo, 70 pages, bibliography and index. Same publisher. $1 net.

The two books are issued by the Johns Hopkins Press on behalf of the Institute for Government Research, which is an association of citizens coöperating with public officials in the scientific study of government with a view to promoting efficiency and economy in public affairs. With this purpose, close and intimate studies are made of the several departments, and in the volumes before us two very important departments are discussed.

The Weather Bureau is very well known to the people of the United States. Its great services to farmer, mariner and shipper are appreciated, though the forecasters come in not infrequently for both serious and flippant criticism. There are now in the United States over 6000 meteorological stations, and it is estimated that over thirty thousand are established in the world. Systematic weather observations were undertaken in the United States in 1870, in connection with the Signal Service, but in 1891, the bureau was transferred to the Department of Agriculture. It is stated that the earliest regularly organized observations were inaugurated by the Duke of Tuscany in 1654. The operation lasted about thirteen years. The publication of forecasts began in the United States on February 19, 1871, being called "probabilities" and the officer in charge of these was dubbed by the newspapers "Old Probabilities." The text of the book covers a large amount of information on the organization and work of the Weather Bureau.

A volume is devoted to the work of Federal Power Commission, which is composed of the Secretaries of War, Interior and Agriculture, having been created in 1920, to exercise a broad administrative function over water-power sites located on the navigable waters, public lands and reservation of the Nation. The extent of the water-power resources of the country, the steady growth of utilization thereof, and the activity of inventors in devising apparatus for such utilization, make the functions of the commission very important. The United States is probably somewhat backward in realizing on its water-power reserves. Foreign engineers have developed this source very extensively. "White coal" is widely used in many European countries. It is estimated that

there is sufficient water-power in the United States to do the work of 500,000,000 tons of coal annually. It is interesting to speculate what advantage would result if any considerable proportion of this substitution could be made. The coal question would be practically eliminated and the smoke nuisance in great part disappear. One of the most important phases of the water-power question is the linking up of the more powerful stations in such a way that power can be distributed over large areas. Surplus stations could be established to take the place of stations temporarily disabled, and also stations at which the supply of power is somewhat intermittent could be erected. In early days the water-driven mill was one of the most familiar objects in the settled area, but the material to be manufactured had to be brought to it and as it was usually located in a somewhat hilly country, the transportations were slow and expensive. Now the water-power machinery may be located in a mountainous region almost inaccessible to ordinary wagons or railroads, as the power can be transmitted with little loss many miles to the most convenient points. The book will be of great interest to industrial chemists and power engineers.

HENRY LEFFMANN.

METALS AND THEIR ALLOYS. A modern practical work dealing with metals from their origin to their useful application—both individually and as parts of alloys—used where strength, ductility, toughness, lightness, color, hardness, cheapness, conductivity, or bearing properties are demanded. By Charles Vickers. Partly based on the third edition of "Metallic Alloys" by William T. Brannt. 767 pages, illustrations, 8vo. New York, Henry Carey Baird and Company, Inc., 1923. Price $7.50.

For many years in the non-ferrous foundry industry, the work of the late William T. Brannt, "Metallic Alloys," has been used as a reference book. It has now been some years since a new edition of Brannt has been published. Vickers recognized the desirability of a thorough revision of Brannt's work and proceeded with that end in view. So numerous were the additions and so completely did the older work require revision, that instead of revising Brannt's work, he has in reality given to the foundry a new work. Mr. Vickers writes from the standpoint of a practical foundryman, being a specialist in melting, alloying and casting metals. He has for a number of years been a technical editor on trade papers connected with the non-ferrous foundry industry.

The first chapter is devoted to a discussion of the elements; the second to a history, production, methods, properties and uses of the elements; the third chapter to alloys, historical, fundamentals, definitions, groups; chapter 4, characteristics of alloys; chapter 5, the art of alloying: melting and combinations. In the following chapters up to chapter 28, he deals with alloys of the common metals. Chapter 28, surface coloring of alloys; chapter 29, foundry utilization of scrap metals; chapter 30, analysis of babbitt metals; chapter 31, foundry data.

The work is considered one of reliability and of good practical value to the foundryman and the manufacturer of alloys.

G. H. CLAMER.

STATISTICAL BIBLIOGRAPHY IN RELATION TO THE GROWTH OF MODERN CIVILIZATION. By E. Wyndham Hulme, B.A., Sandars Reader in Bibliography, Sometime Librarian of the Patent Office. Printed for the author by Butler and Tanner. Grafton and Company, London. Small 4to, 44 pages, tables and charts.

This book contains the substance of two lectures delivered at the University of Cambridge in 1921. It represents an unusual line of investigation. It is an effort to determine what may be called the "moment" of civilization at a given date by an analysis of the bibliography thereof. The inquiry is limited to England, undoubtedly due to the vastness of the subject and to the especial opportunities which the author had through his professional positions. Yet it would seem that the attempt to write the history of civilization by examining British records would be somewhat like attempting to build up a department of natural history by examining the rocks, fauna or flora of limited area. This is not said in derogation of the book, for the ideas upon which it is based are original and the data given are evidently derived by careful and difficult searching. The author, indeed, is conscious of the partial character of the work, and makes special mention of the data that German libraries are said to contain, such as a large collection of works on pyrotechnics, the term being used in a wide sense, and not in our ordinary limit of "fireworks." There is, however, another point to be regarded. How far has the destruction of manuscript affected the record of human literary and scientific activity? The mistake of taking existing material as indexes of the character of a given age has been frequently made in geology and anthropology. Darwin's chapter on the imperfection of the geological record has a value beyond the purpose for which it was written. It is a trite remark that we cannot know the extent of our ignorance, but it is a principle that is often overlooked. Mr. Hulme is an evolutionist. He evidently regards that doctrine as no longer in dispute. He does not expect any radical change in the human race. "Man," he says "represents a type of organism in its approximately final stage." Neither in his mental nor physical structure "has he visibly advanced or receded from the standard to which he is found to conform in the paleolithic age." This is somewhat discouraging, and many biologists and sociologists may take issue with the assertion. Our knowledge of prehistoric man is very scanty. In some periods he evidently had considerable artistic ability, both in painting and sculpture, but this work was almost entirely reproductions of objects with which he was familiar. Of the dramatic, inventive side of art there is little if any record. Yet as regards the *historic* human being, at least, not further back than a few milleniums, it may be said that while the race has gained enormously in knowledge, it has not gained much in wisdom. The basic principles of human action were as familar to the ancient Egyptians, Babylonians, Jews and Greeks as to us. Our notions of the life and work of these peoples are unquestionably seriously restricted by the lack of a large amount of literature that has been destroyed.

Necessarily, the extent of the book enables the author to give only a limited survey of his subject. A list is given of the manuscripts preserved in the British Isles dating not later than 1500. It appears that medical treatises constitute

half of the items of this list, while the art of war, architecture and decorative arts are represented by very few titles. Taken as an index of human activities during that period, it seems to show that by far the most energy was given to healing. Undoubtedly, disease is always with us, and always such as to urge us to secure relief, but the period covered by the list was a period of war, building of castles and churches, and development of many forms of decoration.

As an index of the character and extent of British progress in the applied arts and sciences, a list of British patents from 1561 to 1921 is given in a graph, with comparative population curves. There seems to be a typographic error on page 19, since the chart is there stated to give the patents from 1550 to 1821. In the copy in hand there has also been, apparently, a misbinding of charts, as No. 3 immediately follows No. 1.

A graph is also given of population-increase and issue of patents in the United States from 1850 to 1921. The lines follow pretty closely. There is a distinct peak from 1914 to 1918, which may be in part due to the stimulation in invention in war appliances on account of the extensive introduction of new methods of offence.

A curious fact is mentioned in connection with the beginning of the literature of Technology. "The order of the appearance of this literature is not the order of utility, for the literature of Technology begins with Song, or as we should call it to-day—Didactic Poetry." The reference is to a poem, "Dyer's Fleece," which describes a spinning invention of Lewis Paul a year before it was patented. The author's outlook on the present-day industria' civilization is that "the Age of Power is approaching its natural limits." "Thus, the industrial future of civilization must be in the direction of a gradual transformation of its mineral basis to one founded upon the utilization of natural sources of energy and the building up of products from elements of which there is practically an inexhaustible supply."

The book contains a large amount of original and interesting matter, well worth the attention of the sociologist and historian. The author deserves much credit for the labor he has bestowed on the text, tables and charts, by the preparation of which he has opened a new and useful field of discussion. Necessarily, some of the statements will arouse dissent, and the data presented constitute but a small proportion of what will be needed for definite conclusions.

HENRY LEFFMANN.

REPRINT AND CIRCULAR SERIES OF THE NATIONAL RESEARCH COUNCIL. Fine and Research Chemicals, second revision. Issued by the Committee on Research Chemicals, Clarence J. West, Secretary of the Committee. 45 pages, 8vo, pamphlet. Washington, District of Columbia, Council, 1923.

This list of several thousand rarer chemicals, now made in the United States, is an encouraging indication of the degree to which this country is becoming independent of other nations, especially Germany. A list of firms engaged to a greater or less degree in such manufacture is given, and such firms as sell directly in comparatively small lots are noted, which will be of much use to the ordinary worker. It is reported that biological stains and indicators, which have for a long while been regarded as special German

products, are now made in the United States of fully satisfactory quality. Several of the national societies, of which the members are specially interested in these stains, have joined in forming a committee which will begin very shortly issuing certificates for each stain, which will be marketed with a label stating the accuracy of the sample.

HENRY LEFFMANN.

THE BEVERAGE BLUE-BOOK FOR 1923. 334 pages, 8vo. H. S. Rich and Company, Chicago, 1923.

This is the annual standard directory, buyers' guide and reference volume for the beverage industry of the United States, covering the class commonly termed "soft drinks." This has been for many years a very active business in this country, and since the establishment of prohibition legislation it has greatly increased. Material improvement has taken place on all the details of the manufacture, especially by the introduction of liquefied carbon dioxide. The book contains not only a list of the manufacturers and bottlers of these beverages, of which there is a great variety of types, but some text of special interest to those engaged in the business. Many illustrated and display advertisements show how mechanical ingenuity has been encouraged in connection with the bottling and marketing of the beverages.

HENRY LEFFMANN.

WOOD DISTILLATION. By L. F. Hawley, in charge of section of Derived Products, Forest Products Laboratory. 136 pages, 28 illustrations, 8vo. The Chemical Catalog Company, New York, 1923. Price $3 net.

This is one of the American Chemical Society's Monographs, and in general form and character follows the preceding volumes. It appears from the preface that books in English on wood distillation are few in number and in some cases not of high value. Two works in foreign languages are mentioned as excellent. One is German; the other Swedish. It is much to be regretted that the secondary languages of western Europe are so often used for the medium of valuable scientific data. Of the Scandanavian tongues, Swedish is probably the most difficult. Books written by foreign authorities are always more or less misleading to American workers, and, therefore, the present work, which is the result of large experience and much research in our own operations, will be welcome to American chemists. In colonial days, forests were extensive and trees large. Great waste occurred by the manufacture of charcoal for the iron furnaces, and extensive areas were denuded. In other regions, especially in the Blue Mountains, much deforestation occurred by the cutting of hemlock spruce for the bark, which was used for tanning. In the early manufacture of charcoal, the by-products were not collected, but a distillation industry has developed on account of the demand for certain ingredients of the condensible vapors. Among these are acetic acid, methyl alcohol and acetone. Special woods, such as beech, give a tar containing kreasote. Methyl alcohol was long used as a substitute for ethyl alcohol in many industrial processes, and was, unfortunately, also used in medicinal preparations and beverages, being much cheaper, when the tax was paid on the latter. It is probable that methyl alcohol could not compete with pure, untaxed ethyl alcohol.

Much improvement has taken place in the wood distillation machinery of late years. The demand for crude methyl alcohol as a denaturing material, and the wide market for calcium acetate and charcoal have given impetus to the industry.

The work is in two parts. Destructive distillation of hard woods occupies eighty-two pages, the remainder being devoted to the distillation of resinous woods. A recent and promising development of the procedures is the distillation of sawdust and chips. These materials have several advantages over larger masses. They can be more rapidly and thoroughly dried, are cheaper and can be applied in a continuous process. They are, however, not without some disadvantages which special mechanical methods are necessary to overcome. Wood is a poor conductor of heat, and sawdust is, of course, still poorer. A stirrer or a rotating retort is needed, and the finely divided charcoal is difficult to cool when in large amount, indeed, may be the cause of serious explosions. One company has, however, avoided these disadvantages to a certain extent, by bricketting the sawdust. If heavy pressure is used, a solid mass can be formed without any binding material. Other methods have been devised, which are described in detail. The tar of hard wood distillation has had, as yet, but limited application, although its use is increasing. A special ingredient of beech tar, kreasote, is now prepared in the United States.

Tables of analyses of many woods are given. The data show the progress that has been made in the detection and determination of the more or less complicated proximate principles occurring in vegetable structures. It appears, however, from occasional statements in the text that many data both as to the composition of the raw materials and of the products, as well as details of procedures, remain to be ascertained. In connection with the production of charcoal, attention may be called to the interesting data obtained during the war concerning the conditions under which it acts as an adsorber of gases. This phase of the subject is not within the scope of the work, and is, therefore, not discussed. Information is given as to the refining of the more important volatile products of the distillation.

The second part of the book is devoted to the methods and results of distillation of resinous woods. Two distinct systems are here applied: Destructive distillation and with steam. The methods and apparatus employed in the first form are somewhat various in type. On account of the resinous ingredients, the tar produced floats on the watery portion which contains the pyroligneous acid. The latter is usually a waste product, the valuable ingredients being in the tar, from which volatile oils of the turpentine class are derived. Steam distillation has the advantage that much smaller pieces of wood may be used. Turpentine and rosin are the most valuable products of this procedure. The yields are of better quality than those of the destructive distillation. One product, steam distilled pine oil, comparatively new to the market, was at first not well received, but is now finding many applications.

The book is filled with important and interesting information, and not the least value of it are the indications that it offers for research in the line of industrial applications of wood products.

HENRY LEFFMANN.

THÉORIE DES NOMBRES. Par M. Kraïtchik, Ingénieur à la Société Financière des Transports et d'Entreprises industrielle, Directeur à l'Institut des Hautes Études de Belgique avec une préface de M. d'Ocagne. ix + 229 pages, 6½" × 9½". Paris, Gauthier-Villars et Cie., 1922. Price, in paper, 25 Francs.

The present work is an account of the elements of the theory of numbers and constitutes an introduction to the further development of the theory. It is the intention of the author in succeeding volumes to prosecute derived theories, but as far as the subject is covered, even this first volume will render valuable service to all who are interested in the various investigations of numbers.

Mr. Kraïtchik's contribution to the subject is to have conceived the most reliable, the easiest and quickest methods possible of "sieving" or elimination processes upon groups of numbers of such magnitude as to discourage the application of all usual tentative methods. Whereas the usual "sieving" processes could scarcely be practically applied to more than thirty or forty possible values, that of Mr. Kraïtchik permits, with no greater expenditure of labor or time, the application of the operation to groups comprising several millions and even several tens of millions of numbers, without which, thanks to an effective graphic plan, it would be necessary to write out those numbers. Mr. Kraïtchik has gone even further; he has outlined the elements of a mechanism by the aid of which the process of "sieving" may be effected by the use of a special calculating machine.

LES APPLICATIONS ÉLÉMENTAIRES DES FONCTIONS HYPERBOLIQUES À LA SCIENCE DE L'INGÉNIEUR ÉLECTRICIEN. Par A. E. Kennelly, Professeur d'Électricité appliquée, Université de Harvard, Directeur des Recherches électriques appliquées, Massachusetts Institute of Technology, Professeur américain d'Échange auprés des Universités françaises 1921–22. viii–153 pages, 6½ × 9½ inches, paper. Paris, Gauthier-Villars et Cie., 1922. Price, 15 Francs.

There is undoubtedly greater inclination in Continental Europe to translate into the language of the country important technical works than exists in English-speaking countries, and the lack of English translations of certain important foreign technical works has been often a matter of comment.

At the first glance upon the title and authorship of this work with the make-up of the familiar cover-page of its noted publishers, the first impression is that with their usual appreciation of technical merit, they have issued a translation of the distinguished author's account of his highly original mathematical devices which eliminate so much of the labor entailed in alternating current transmission lines. Upon a closer view, it is not a mere translation, but a distinct work in French by Doctor Kennelly himself.

During the scholastic year 1921–1922, Doctor Kennelly was among the leading scientists chosen to represent seven eastern universities in the exchange professorship movement. In issuing his lectures in the language of the country in which they were delivered, the author has adopted a graceful means of acknowledging the appreciation and cordial reception of his French auditors.

LA COMPOSITION DE MATHÉMATIQUES DANS L'EXAMEN D'ADMISSION À L'ÉCOLE POLYTECHNIQUE DE 1901 À 1921. Par F. Michel, Ancien élève de l'École Polytechnique, Licencié ès Sciences Mathématiques, Ingénieur Chef des Services électriques du Chemin de fer du Nord, et M. Potron, Ancien élève de l'École Polytechnique, Docteur ès Sciences Mathématiques. xii–452 pages, 6½″ × 9½″. Paris, Gauthier-Villars et Cie., 1922. Price, in paper, 40 Francs.

In publishing this new collection of problems in mathematics given in the competition, examinations for entrance to the École Polytechnique for 1901 to 1920, the authors warn the user not to expect from their study a panacea for passing a successful examination. Nevertheless, there is profit as well as comfort for a prospective candidate to be derived from a set of such papers, covering a term of years, with solutions to the problems.

The object of this examination is not alone to test the students' knowledge of fundamental processes, but also his ability to apply them, a point of great importance in determining mathematical aptitude. The mode of attack is indeed only second in importance to thorough grounding in mathematical processes and dexterity in algebraic transformation. With that object, the questions, more often than not, are presented without regard to classification of the processes which are to be employed in their solution. Further, another question is often derived from a preceding one, and book-rote is replaced by a test of professional capacity.

The work is in two separate parts. The first part consists of the examination questions with their solution and explanation. In the second part, in the order in which the various topics of the course have been presented, specific problems occurring in the first part are discussed. The scope of the subject matter is substantially similar to that offered in the science courses in American universities. These entrance requirements cover what in this country is required for post-graduate study in this subject. When it is considered that the two years' course at the École Polytechnique is prerequisite to entrance, to such special professional schools as the École Nationale Supérieur des Mines or the École des Ponts et Chaussées, it is evident that a high order of scholarship is expected in professional study "over there."

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 158, Mathematical Equations for Heat Conduction in the Fins of Air-cooled Engines. By D. R. Harper, 3rd, and W. B. Brown. 32 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This report deals with the problem of reducing actual geometrical area of fin-cooling surface, which is, of course, not uniform in temperature, to equivalent "cooling" area at one definite temperature, namely, that prevailing on the cylinder wall at the point of attachment of the fin. This makes it possible to treat all the cooling surface as if it were part of the cylinder wall and 100 per cent. effective.

The quantities involved in the equations are the geometrical dimensions of the fin, thermal conductivity of the material composing it, and the coefficient of surface heat dissipation between the fin and the air stream. Several assumptions of a physical nature are thus necessarily involved in making the

problem possible of solution. These are set forth in detail, and the limitations which result from them in applying the equations to numerical calculation are carefully pointed out.

An expression for approximate fin effectiveness is developed, based upon simple mathematics and very convenient in form for engineering use. The essence of the paper is an examination into the magnitude of the errors involved in using this expression without correction and a determination of the corrections needed for accurate work. The mathematical expressions involved are quite complicated, including Fourier's series, super-Fourier's series, Bessel functions of zero order of two kinds with imaginary arguments, etc. The results of the work are collected in graphical form in a series of charts, so that the design engineer can use the simple formula first developed and apply to it corrections readily read from the charts, thus avoiding entirely all higher mathematics.

Report No. 159, Jet Propulsion for Airplanes. By Edgar Buckingham. 18 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This report is a description of a method of propelling airplanes by the reaction of jet propulsion.

Air is compressed and mixed with fuel in a combustion chamber, where the mixture burns at constant pressure. The combustion products issue through a nozzle, and the reaction of the jet constitutes the thrust.

Data are available for an approximate comparison of the performance of such a device with that of the motor-driven air screw. The computations are outlined and the results given by tables and curves.

The relative fuel consumption and weight of machinery for the jet decrease as the flying speed increases; but at 250 miles per hour the jet would still take about four times as much fuel per thrust horsepower-hour as the air screw, and the power plant would be heavier and much more complicated.

Propulsion by the reaction of a simple jet cannot compete, in any respect, with air screw propulsion at such flying speeds as are now in prospect.

Report No. 162, Complete Study of the Longitudinal Oscillation of a VE-7 Airplane. By F. H. Norton and W. G. Brown. Five pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This investigation was carried out by the National Advisory Committee for Aeronautics at Langley Field in order to study as closely as possible the behavior of an airplane when it was making a longitudinal oscillation. The air speed, the altitude, the angle with the horizontal and the angle of attack were all recorded simultaneously and the resulting curves plotted to the same time scale. The results show that all curves are very close to damped sine curves, with the curves for height and angle of attack in phase, that for angle with the horizon leading them by 18 per cent. and that for the path angle leading them by 25 per cent.

Report No. 164, The Inertia Coefficients of an Airship in a Frictionless Fluid. By H. Bateman. 16 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

Report No. 164 deals with the investigation of the apparent inertia of an airship hull. The exact solution of the aerodynamical problem has been studied

for hulls of various shapes and special attention has been given to the case of ellipsoidal hull. In order that the results for this last case may be readily adapted to other cases, they are expressed in terms of the area and perimeter of the largest cross-section perpendicular to the direction of motion by means of a formula involving a coefficient K which varies only slowly when the shape of the hull is changed, being 0.637 for a circular or elliptic disc, 0.5 for a sphere, and about 0.25 for a spheroid of fineness ratio 7. For rough purposes it is sufficient to employ the coefficients, originally found for ellipsoids, for hulls otherwise shaped. When more exact values of the inertia are needed, estimates may be based on a study of the way in which K varies with different characteristics and for such a study the new coefficient possesses some advantages over one which is defined with reference to the volume of fluid displaced.

The case of rotation of an airship hull has been investigated also and a coefficient has been defined with the same advantages as the corresponding coefficient for rectilinear motion.

Report No. 167, The Measurement of the Damping in Roll on a JN4h in Flight. By F. H. Norton. 6 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This investigation was carried out by the Committee for the purpose of measuring the value of L_p in flight. The method consisted in flying with heavy weights on each wing tip, suddenly releasing one of them, and allowing the airplane to roll up to 90° with controls held in neutral while a record was being taken of the air speed, and angular velocity about the X-axis. The results are of interest as they show that the damping found in the wind-tunnel by the method of small oscillations is in general 40 per cent. higher than the damping in flight. At 50 m.p.h. the flight curve of L_p has a high peak, which is not indicated in the model results. It is also shown that at this speed the lateral manœuverability is low.

U. S. COAST AND GEODETIC SURVEY. Terrestrial Magnetism. Horizontal Intensity Variometers. By George Hartnell (Special Publication No. 89). Sixty-two pages, illustrations, plate, 8vo. Washington, Government Printing Office, 1922. Price, 10 cents.

A variometer is an instrument containing a suspended or supported magnet which is free to move under the action of a varying magnetic field. The magnet is placed at right angles to that particular component of the field which is being investigated. Magnetic observatories are equipped with a set of three variometers collectively called a magnetograph. The D variometer indicates changes in *declination*. The Z variometer indicates changes in the *vertical intensity*. The theory of the Z variometer was discussed in the *Journal of Terrestrial Magnetism and Atmospheric Electricity*, June, 1919.

This publication treats of the characteristics of the third variometer of the magnetograph, namely, the *horizontal intensity variometer*. The paper is divided into two parts. Part I deals with the theory of the horizontal intensity variometer proper, and discusses in considerable detail the characteristics of the bifilar and unifilar variometers, and also characteristics common to both.

Part II is a study of the two types of suspension. As an indication of the nature of the discussion, one characteristic is selected for special mention.

The magnet suspended by a quartz fibre under torsion is unequally deflected and the field is increased and decreased by equal amounts, consequently the horizontal intensity variometer in which the magnet is held perpendicular to the field by the torsion in the fibre is less sensitive when the field increases than when it decreases, that is, the scale value is greater for ordinates indicating a larger field intensity. The inequality is so large in unifilar quartz suspensions as to necessitate a correction to the variometer. Its magnitude is determined by the coefficients in a series of developments of the scale value in powers of the ordinates. It is shown how this inequality in scale value can be eliminated and a constant uniform scale value secured by means of a fibre of suitable size and a control magnet to reduce the scale value to the desired amount.

The publication treats the subject of horizontal intensity variometers in a comprehensive manner and will prove of value to those operating or designing these instruments.

PUBLICATIONS RECEIVED.

Statistical Bibliography in Relation to the Growth of Modern Civilization. Two lectures delivered in the University of Cambridge in May, 1922, by E. Wyndham Hulme, B.A., Sandars Reader in Bibliography, Sometime Librarian of the Patent Office. 44 pages, tables, charts, quarto. London, printed for the author by Butler and Tanner, 1923.

Wood Distillation, by L. F. Hawley. American Chemical Society Monograph Series. 141 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1923. Price $3.

Mirrors, Prisms and Lenses. A textbook of geometrical optics by James P. C. Southall. Enlarged and revised edition. 657 pages, illustrations, 12mo. New York, The Macmillan Company, 1923.

The Beverage Blue Book, 1923. The Standard Directory, Buyers' Guide and Reference Volume for the Beverage Industry. 324 pages, illustrations, 8vo. Chicago, H. S. Rich and Company, 1923.

National Advisory Committee for Aeronautics: Technical Notes No. 149, Influences in the Selection of a Cycle for Small High-speed Engines Running on Solid or Airless Injection with Compression Ignition, by Robertson Matthews. 11 pages, illustrations, quarto. Washington, District of Columbia, Committee, July, 1923.

Animal-eating Plants. HEBER W. YOUNGKEN, of the Philadelphia College of Pharmacy and Science (*Amer. Jour Pharm.*, 1923, xcv, 329-350), states that approximately 500 species of green plants are carnivorous or animal-eating. Their leaves have become modified to allure, capture, imprison, digest and absorb their prey. The chief carnivorous plants are the sun-dews, fly-traps, pitcher-plants, bladderworts, and butterworts. J. S. H.

CURRENT TOPICS.

The Reaction Consequent upon the Evaporation of a Liquid and upon the Emission of Vapors from Small Orifices. W. G. DUFFIELD. (*Phil. Mag.*, April, 1923.)—The original problem which the author set out to solve was "whether in the process of evaporation or boiling into the open air, there were any measurable mechanical reaction upon the surface from which the molecules were issuing." Ether in a covered crystallizing dish was put on the pan of a balance and equipoised. Upon the removal of the cover the liquid began to evaporate but no downward recoil of the liquid due to the projection of molecules upward manifested itself. From the rate of evaporation and the normal velocity of molecules of ether vapor at the temperature of the experiment this recoil should have amounted to .054 gram weight, but it did not exist. Later, on a balance pan 3.20 gms. water were boiled away in 20 secs. Theory would indicate that the consequent downward thrust should amount to 11.4 grs., a weight equal to several times that of the water. The pan with the water should not have risen, but as a matter of fact it did, owing to the disappearance of the water. Manifestly there is something wrong with the theory, for the force of recoil could have been detected had it been even one-hundredth as great as it was computed to be. "Is it absent because the general view is wrong that the molecules issue with the velocity we have assigned to them; do they instead of being projected like bullets just drop off? Do they suffer so much in velocity in penetrating the surface layer?" An experiment was made which showed that the recoil exists and manifests itself when evaporation takes place, not into air or other gas or vapor, but into a vacuum. This goes to prove that the molecules start away from the liquid with high velocities and that in some manner it is the presence of the gas or vapor above which causes the looked-for reaction to fail to appear. "There is some compensating interaction between the projected molecules and the molecules of air or previously evaporated material in the space above the liquid, which prevents the loss of momentum of the projected material from becoming evident as a pressure upon the surface." To clarify the problem the author proposes an analogy. Let there be a gun platform carrying a thousand cannon each shooting a ball in the same horizontal direction once a second. The reaction on the platform would be the same, no matter whether the balls went into a near-by sand bank or passed out of sight. This represents the case without complications. Any evaporating liquid not in vacuo has beating on its surface a procession of molecules from the space above it. "It is as though our gun platform were being bombarded by enemy fire, which we can picture as occasioning a pressure which might be measured by the com-

pression of a spring. Upon our opening fire, there is an additional reaction if our cannon balls do not strike those of the enemy (*i.e.*, if the cannon ball density is low), but if they do collide in such a way that each ball stops or diverts an enemy ball, the reading of the sprig will remain unaffected by the discharge of our guns, since each discharge both contributes a certain amount of kick to the platform and robs it of the impact of an enemy shell. But it is not infinitely probable that each enemy shell will meet one of ours in such a way as to be prevented from delivering its momentum to the platform, so that the neutralization is not likely to be complete unless the discharge rate is very great," that is, unless the enemy fire is heavier than ours, so that each of our shots shall meet a hostile ball. If we want to notice the recoil, our fire must exceed that of the enemy so that many of our balls shall get away without having struck an oncoming projectile. And this is later shown to be true in the case of jets of steam.

Let him who thinks himself well informed in matters of evaporation and boiling read this paper that he may recognize his ignorance.

G. F. S.

The True Oil-bearing Milkweeds.—Note was made in a recent issue of this JOURNAL of the extraction of oil from the seeds of several species of *Asclepias*, commonly known as milkweeds. The note was based on an article in the *Bull. d. Mat. Gras.* of Marseilles. It appears that the editor of that publication was misled by the term milkweed, and that the plant from which the oil is obtained is the Mexican poppy, *Argemone mexicana*. This is a member of the Papaveraceæ, the family to which the opium plant and the now famous Flanders poppy belong. Many of the plants of this group have a milky juice, so that they may be called milkweeds in some localities. In some species, however, the juice is highly colored, as in the common celandine. The account given by the French journal was probably taken from Spanish sources. An abstract in English is given in the initial number of the new series of the *International Review of Science and Practice of Agriculture*, p. 216. The constants of the oil are given in detail.

H. L.

First Annual Report of the International Committee on Chemical Elements.—For a number of years an international committee on atomic weights was engaged in compiling data concerning revisions of atomic weight determinations, publishing annually a table of approved figures. This committee was appointed by the International Association of Chemical Societies, which was broken up by the war, and the operations of its committees temporarily suspended. After the war closed, the representatives of several of the nations that had been allied against the Central Powers formed the International Union of Pure and Applied Chemistry, which created a committee designated as the International Committee on Chemical Ele-

ments. The change of title and scope is rendered necessary by the great progress in the field of isotopy, first recognized in connection with the radioactive elements, but now extended to many other groups. The duty of the committee will be to keep chemists informed of the progress of discovery in this promising field. It consists at present of eight members representing United States, Great Britain, France and Czecho-Slovakia. Germany and Austria have not yet been taken into the fold. In addition to constituent members the committee has special experts and two honorary presidents.

Under these auspices a first report has been issued containing tables of isotopes and radioactive elements. The committee considers that its work in this field is only provisional. Recognizing that the definitions and nomenclatures adopted are not homogeneous, the committee regards some changes as necessary, but, pending general approval, has made only a few modifications and has deemed it proper to submit these to the judgment of the discoverers. The names "radon," "actinon," and "thoron" were, therefore, submitted to Rutherford and Curie, and as these names are given in the tables, it is presumed that they have been approved.

The following definitions are taken from the report:

A chemical element is defined by its atomic number. This number represents the excess of positive over negative charges in the constitution of the atomic nucleus. Theoretically, the atomic number also represents the number of electrons which rotate around the central positive nucleus of the atom. Each atomic number represents the place occupied by the element in the Mendeleef table. If the above definition is accepted, elements may be simple or complex, according as their atoms are all of the same mass or not. Complex elements consist of as many isotopes as its atoms have different masses, therefore, consist of a mixture of isotopes. All elements considered as units are represented by their standard symbol, but to represent isotopes, the symbol is modified by an exponent indicating the mass of the given isotopes. In the English text, this exponent is written as a superior, for example, Cl^{35} refers to the chlorine isotope having the atomic mass of 35. In the French text (the report is bilingual) the isotope is represented by Cl_{35}. This is probably due to the fact that French chemists use the old form of exponent, written as a superior and, therefore, just reverse the methods followed by all other nations, but this practice is slowly disappearing and it is to be hoped that uniformity may be soon attained. In establishing the mass of the isotope, oxygen is, as usual, taken as 16. The isotopes of lead which are the ultimate result of disintegration of radioactive elements and the radioactive isotopes will alone appear in the international table of radioactive elements. The expression "atomic mass" is reserved for isotopes or simple elements considered from the isotopic point of view. The expression "atomic weight" retains its usual meaning, and is applied to elements without consideration of their isotopic constitution.

The pamphlet contains a table of over thirty elements, mostly the abundant ones, with several data, among which the most interesting is the statement of the number of isotopes so far elucidated. Lithium is the element of lowest atomic weight that is given as having isotopes, consisting of two with respective masses of 6 and 7. Boron has two, respectively, 10 and 11. Silicon is given two (28 and 29) with provisionally a third (30). Selenium is given six and tin seven with a possible eighth. Xenon is given seven with possibly two more. A large table is appended, giving the three series of radioactive elements, *viz.*, uranium-radium series, ending with radium Ω' which is isotopic lead, the actinium series and the series of thorium, which last also ends with lead (Th Ω'), but the lead terminating the radium series has a different atomic mass (that is, is a different isotope) from that ending the thorium series, the former being Pb^{206}, the latter Pb^{208}.

An inspection of the table will show the extraordinary development that has taken place in the knowledge of the nature and properties of the chemical elements. H. L.

The Ionization of Potassium Vapor by Light. R. C. WILLIAMSON. (*Phys. Rev.*, Feb., 1923.)—"Experimental results relative to the ionization of metallic vapors by light have been very meagre, and it is difficult to point to any phenomena which are due, without doubt, to ionization by radiation of optical frequencies." In this paper evidence from experiment is presented that potassium vapor is actually ionized by ultra-violet light. "This ionization begins with wave-lengths of about 3000 Å., and increases rapidly and continuously in amount as the wave-length of the exciting radiation decreases from 3000 to 1850 Å., the limits investigated. The number of atoms exposed for a second to a given intensity of radiation, per electron ejected from an atom, is of the same order of magnitude in the solid as in the vapor state, for wave-length regions corresponding to marked sensitivities in each case. For the intensities used in these experiments, this number was about 10^5." G. F. S.

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